

When the capacitor 128 has been charged to the desired voltage, the control circuit 122 turns OFF current sinks 124 and 126. Again, with proper selection of the size of the series resistor 142, transistor 140 will clamp off the converter and then assume a

standby state in which it draws no power. If a noise pulse of negative polarity and sufficient magnitude occurs at the base of transistor 118, transistors 118 and 140 turn ON and the base-emitter voltage of transistor 118 is clamped at a level which is insufficient to drive the transistor 118 into heavy conduction. With the base drive to the transistor 118 clamped at low level, the converter again turns OFF when the noise pulse terminates and the clamp transistor 140 again assumes the standby-by state.

Figure 3 shows a clamp device having JFET 250 connected in Darlington configuration to the clamp transistor 218. The use of a JFET has the advantage of allowing the use of a low current clamp current sink 226.

Figure 4 shows a clamp device having an additional PNP driver transistor 352 coupled between the base circuit of a clamp transistor 318 and the transformer oscillating transistor (not shown). The transistor 352 provides a very low impedance temporary clamp pulse to the oscillating transistor, which in turn provides very rapid turn OFF of the converter.

Disclosed by Gregory Oscar Moberg and Lynn Robert Hudson
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Sensitized high aspect ratio silver halide emulsions and photographic elements

High aspect ratio chemically and spectrally sensitized tabular grain silver halide emulsions, photographic elements incorporating these emulsions, and processes for the use of the photographic elements are disclosed. In the tabular grain emulsions the silver halide grains having a thickness of less than 0.5 micron, preferably less than 0.3 micron, and preferably a diameter of at least 0.6 micron have an average aspect ratio of at least 5:1 and account for at least 50 percent of the total projected area of the silver halide grains present.

Photography, since its emergence as a practical art in the last half of the nineteenth century, has relied upon elements containing radiation-sensitive silver halide to serve a wide range of imaging needs. As compared to available imaging alternatives, silver halide photographic elements exhibit a combination of very advantageous properties, including higher speed and better image definition. Further, silver halide photographic elements are virtually unique in their highly refined capability for accurately reproducing multi-color images.

Over the last century silver halide photographic elements have retained their prominent position in the photographic industry by reason of intensive and painstaking investigations, both theoretically and empirically based, aimed at better understanding and improving photographic capabilities. Extensive academic and industrial research has been devoted to the improvement of silver halide photographic elements, and thousands of patents have been issued, attesting to the vigor with which improvement has been pursued.

Silver halide photography employs radiation-sensitive emulsions comprised of a dispersing medium, typically gelatin, containing embedded microcrystals — known as grains — of radiation-sensitive silver halide. During imagewise exposure a latent image center, rendering an entire grain selectively developable, can be produced by absorption of only a few quanta of radiation, and it is this capability that imparts to silver halide photography exceptional speed capabilities as compared to many alternative imaging approaches.

The sensitivity of silver halide emulsions has been improved by sustained investigation for more than a century. A variety of chemical sensitizations, such as noble metal (eg, gold), middle chalcogen (eg, sulfur and/or selenium), and reduction sensitizations, have been developed which, singly and in combination, are capable of improving the sensitivity of silver halide emulsions. When chemical sensitization is extended beyond optimum levels, relatively small increases in speed are accompanied by sharp losses in image discrimination (maximum density minus minimum density) resulting from sharp increases in fog (minimum density). Optimum chemical sensitization is the best balance among speed, image discrimination, and minimum density for a specific photographic application.

Usually the sensitivity of the silver halide emulsions is only negligibly extended beyond their spectral region of intrinsic sensitivity by chemical sensitization. The sensitivity of silver halide emulsions can be extended over the entire visible spectrum and beyond by employing spectral sensitizers, typically methine dyes. Emulsion sensitivity beyond the region of intrinsic sensitivity increases as the concentration of spectral sensitizer increases up to an optimum and generally declines rapidly thereafter. (See Mees, *Theory of the Photographic Process*, Macmillan, 1942, pp 1067-1069, for background).

Within the range of silver halide grain sizes normally encountered in photographic elements the maximum speed obtained at optimum sensitization increases linearly with increasing grain size. The number of absorbed quanta necessary to render a grain developable is substantially independent of grain size, but the density that a given number of grains will produce upon development is directly related to their size. If the aim is to produce a maximum density of 2, for example, fewer grains of 0.4 micron as compared to 0.2 micron in average diameter are required to produce that density. Less radiation is required to render fewer grains developable.

Unfortunately, because the density produced with the larger grains is concentrated at fewer sites, there are greater point-to-point fluctuations in density. The viewer's perception of point-to-point fluctuations in density is termed 'graininess'. The objective measurement of point-to-point fluctuations in density is termed 'granularity'. While quantitative measurements of granularity have taken different forms, granularity is most commonly measured as rms (root mean square) granularity, which is defined as the standard deviation of density within a viewing microaperture (eg, 24 to 48 microns). Once the maximum permissible granularity (also commonly referred to as grain, but not to be confused with silver halide grains) for a specific emulsion layer is identified, the maximum speed which can be realized for that emulsion layer is also effectively limited.

From the foregoing it can be appreciated that over the years intensive investigation in the photographic art has rarely been directed toward obtaining maximum photographic speed in an absolute sense, but, rather, has been directed toward obtaining maximum speed at optimum sensitization while satisfying practical granularity or grain criteria. True improvements in silver halide emulsion sensitivity allow speed to be increased without increasing granularity, granularity to be reduced without decreasing speed, or both speed and granularity to be simultaneously improved. Such sensitivity improvement is commonly and succinctly referred to in the art as improvement in the speed-granularity relationship of an emulsion.

The importance of speed-granularity relationship in photography has led to extensive efforts to quantify and generalize speed-granularity determinations. It is normally a simple matter to compare precisely the speed-granularity relationships of an emulsion series differing by a single characteristic, such as silver halide grain size. The speed-granularity relationships of photographic products which produce similar characteristic curves are often compared. However, universal quantitative speed-granularity comparisons of photographic elements have not been achieved, since speed-granularity comparisons become increasingly judgmental as other photographic characteristics differ. Further, comparisons of speed-granularity relationships of photographic elements which produce silver halide images (eg, black-and-white photographic elements) with those which produce dye images (eg, color and chromogenic photographic elements) involve numerous considerations other than the silver halide grain sensitivities, since the nature and origin of the materials producing density and hence accounting for granularity are much different. For elaboration of granularity measurements in silver and dye imaging attention is directed to 'Understanding Graininess and Granularity', Kodak Publication No F-20, Revised 11-79 (available from Eastman Kodak Company, Rochester, New York 14650); Zwick, 'Quantitative Studies of Factors Affecting Granularity', *Photographic Science and Engineering*, Vol 9, No 3, May-June, 1965; Ericson and Marchant, 'RMS Granularity of Monodisperse Photographic Emulsions', *Photographic Science and Engineering*, Vol 16, No 4, July-August 1972, pp 253-257; and Trabka, 'A Random-Sphere Model for Dye Clouds', *Photographic Science and Engineering*, Vol 21, No 4, July-August 1977, pp 183-192.

While granularity, because of its relationship to speed, is often a focal point of discussion relating to image quality, image sharpness can be addressed independently. Some factors which influence image sharpness, such as lateral diffusion of imaging materials during processing (sometimes termed 'image smearing'), are more closely related to imaging and processing materials than the silver halide grains. On the other hand, because of their light scattering properties, silver halide grains themselves primarily affect sharpness during imagewise exposure. It is known in the art that silver halide grains having diameters in the range of from 0.2 to 0.6 micron exhibit maximum scattering of visible light.

Loss of image sharpness resulting from light scattering generally increases with increasing thickness of a silver halide emulsion layer. In multicolor photographic elements containing three or more superimposed silver halide emulsion layers an increased risk of reduction in image sharpness can be presented, since the silver halide grains are distributed over at least three layer thicknesses. In some applications thickness displacement of the silver halide grains is further increased by the presence of additional materials that either (1) increase the thicknesses of the emulsion layers themselves — as where dye-image-providing materials, for example, are incorporated in the emulsion layers or (2) form additional layers separating the silver halide emulsion layers, thereby increasing their thickness displacement — as where separate scavenger and dye-

image-providing material layers separate adjacent emulsion layers. Thus, there is a substantial opportunity for loss of image sharpness attributable to scattering. Because of the cumulative scattering of overlying silver halide emulsion layers, the emulsion layers farther removed from the exposing radiation source can exhibit very significant reductions in sharpness.

Silver bromide and silver bromiodide emulsions possess sufficient native sensitivity to the blue portion of the spectrum to record blue radiation without blue spectral sensitization. When these emulsions are employed to record green and/or red (minus blue) light exposures, they are corresponding spectrally sensitized. In black-and-white and monochromatic (eg chromogenic) photography the resulting orthochromatic or panchromatic sensitivity is advantageous.

In multicolor photography, the native sensitivity of silver bromide and silver bromiodide in emulsions intended to record blue light is advantageous. However, when these silver halides are employed in emulsion layers intended to record exposures in the green or red portion of the spectrum, the native blue sensitivity is an inconvenience, since response to both blue and green light or both blue and red light in the emulsion layers will falsify the hue of the multicolor image sought to be reproduced.

In constructing multicolor photographic elements using silver bromide or silver bromiodide emulsions the color falsification can be analyzed as two distinct concerns. The first concern is the difference between the blue speed of the green or red recording emulsion layer and its green or red speed. The second concern is the difference between the blue speed of each blue recording emulsion layer and the blue speed of the corresponding green or red recording emulsion layer. Generally in preparing a multicolor photographic element intended to record accurately image colors under daylight exposure conditions (eg 5500°K) the aim is to achieve a difference of about an order of magnitude between the blue speed of each blue recording emulsion layer and the blue speed of the corresponding green or red recording emulsion layer. The art has recognized that such aim speed differences are not readily realized using silver bromide or silver bromiodide emulsions unless employed in combination with one or more approaches known to ameliorate color falsification. Even then, full order of magnitude speed differences have not always been realized in product. However, even when such aim speed differences are realized, further increasing the separation between blue and minus blue speeds will further reduce the recording of blue exposures by layers intended to record minus blue exposures.

Improvements in the above discussed and other photographic properties can be obtained with a radiation-sensitive high aspect ratio tabular grain silver halide emulsion comprised of a dispersing medium and silver halide grains, wherein at least 50 percent of the total projected area of the silver halide grains is provided by chemically and spectrally sensitized tabular silver halide grains having a thickness of less than 0.5 micron, preferably, but optionally, a diameter of at least 0.6 micron, and an average aspect ratio of greater than 5:1.

This disclosure describes such emulsions as well as photographic element comprised of a support and at least one radiation-sensitive emulsion layer comprised of a radiation-sensitive emulsion as described above.

This disclosure also describes producing a visible photographic image by processing in an aqueous alkaline solution in the presence of a developing agent an imagewise exposed photographic element as described above.

Sharpness of photographic images can be improved by employing emulsions according to the present disclosure, particularly those of large average grain diameters. When spectrally sensitized outside the portion of the spectrum to which they possess native sensitivity, the emulsions of the present disclosure exhibit a large separation in their sensitivity in the region of the spectrum to which they possess native sensitivity, as compared to the region of the spectrum to which they are spectrally sensitized. Minus blue sensitized silver bromide and silver bromiodide emulsions according to the disclosure are much less sensitive to blue light than to minus blue light and can, without filter protection, provide acceptable minus blue exposure records when exposed to neutral light, such as daylight at 5500°K. The emulsions of the present disclosure, particularly the silver bromide and silver bromiodide emulsions, exhibit improved speed-granularity relationships as compared to the best speed-granularity relationships heretofore achieved with silver halide emulsions of like halide content generally. Very large increases in blue speed of the silver bromide and silver bromiodide emulsions of the present disclosure have been realized as compared to their native blue speed when blue spectral sensitizers are employed.

Image transfer film units containing emulsions according to the present disclosure are capable of achieving a higher ratio of photographic speed to silver coverage (ie, silver halide coated per unit area), faster access to a viewable transferred image, and higher contrast of transferred images with less time of development. The image transfer film units are capable of producing images of increased sharpness. The film units are particularly advantageous in permitting more efficient use of dye image formers, more advantageous layer order arrangements, elimination or reduction

of yellow filter materials, and less image dependence on temperature.

Black-and-white photographic elements according to the present disclosure exhibit higher covering power in producing silver images. Further, high levels of covering power can be realized with fully forehardened elements.

This can be advantageously applied to radiographic elements. The use of emulsions according to the present disclosure in radiographic elements coated on both major surfaces of a radiation transmitting support can control crossover. Comparisons of radiographic elements containing emulsions according to this disclosure with similar radiographic elements containing conventional emulsions show that reduced crossover can be attributed to the disclosed emulsions. Alternatively, comparable crossover levels can be achieved with the emulsions of the present disclosure using reduced silver coverages.

The emulsions of the present disclosure also exhibit distinct advantages in processing. More rapid processing is generally contemplated with less temperature dependence. The fixing of tabular grains herein disclosed is more rapid than when comparable quantities of silver halide in nontabular or lower aspect tabular grain form is fixed. The high aspect ratio tabular grain silver chlorobromide emulsions can be processed more rapidly than corresponding converted halide silver chlorobromide emulsions.

This disclosure relates particularly to chemically and spectrally sensitized high aspect ratio tabular grain silver halide emulsions, to photographic elements which incorporate these emulsions, and to processes for the use of the photographic elements. As applied to the silver halide emulsions of the present disclosure the term 'high aspect ratio' is herein defined as requiring that the silver halide grains having a thickness of less than 0.3 micron and a diameter of at least 0.6 micron have an average aspect ratio of greater than 8:1 and account for at least 50 percent of the total projected area of the silver halide grains.

The preferred high aspect ratio tabular grain silver halide emulsions of the present disclosure are those wherein the silver halide grains having a thickness of less than 0.3 micron (optimally less than 0.2 micron) and a diameter of at least 0.6 micron have an average aspect ratio of at least 12:1 and optimally at least 20:1. In a preferred form of the disclosure these silver halide grains satisfying the above thickness and diameter criteria account for at least 70 percent and optimally at least 90 percent of the total projected area of the silver halide grains.

It is appreciated that the thinner the tabular grains accounting for a given percentage of the projected area, the higher the average aspect ratio of the emulsion. Typically the tabular grains have an average thickness of at least 0.03 micron, although even thinner tabular grains can in principle be employed — eg, as low as 0.01 micron, depending on halide content. It is recognized that the tabular grains can be increased in thickness to satisfy specialized applications. For example, this disclosure contemplates the use of tabular grains having thicknesses up to 0.5 micron, in photographic applications in which enlargement is not normally undertaken. Grain thicknesses of up to 0.5 micron are also discussed below for recording blue light. (For such applications all references to 0.3 micron in reference to aspect ratio determinations should be adjusted to 0.5 micron). However, to achieve high aspect ratios without unduly increasing grain diameters, it is normally contemplated that the tabular grains of the emulsions of this disclosure will have an average thickness of less than 0.3 micron.

The grain characteristics described above of the silver halide emulsions of this disclosure can be readily ascertained by procedures well known to those skilled in the art. As employed herein the term 'aspect ratio' refers to the ratio of the diameter of the grain to its thickness. The 'diameter' of the grain is in turn defined as the diameter of a circle having an area equal to the projected area of the grain as viewed in a photomicrograph or an electron micrograph of an emulsion sample. From shadowed electron micrographs of emulsion samples it is possible to determine the thickness and diameter of each grain and to identify those tabular grains having a thickness of less than 0.3 micron and a diameter of at least 0.6 micron. From this the aspect ratio of each such tabular grain can be calculated, and the aspect ratios of all the tabular grains in the sample meeting the less than 0.3 micron thickness and at least 0.6 micron diameter criteria can be averaged to obtain their average aspect ratio. By this definition the average aspect ratio is the average of individual tabular grain aspect ratios. In practice it is usually simpler to obtain an average thickness and an average diameter of the tabular grains having a thickness of less than 0.3 micron and a diameter of at least 0.6 micron and to calculate the average aspect ratio as the ratio of these two averages. Whether the averaged individual aspect ratios or the averages of thickness and diameter are used to determine the average aspect ratio, within the tolerances of grain measurements contemplated, the average aspect ratios obtained do not significantly differ. The projected areas of the tabular silver halide grains meeting the thickness and diameter criteria can be summed, the projected areas of the remaining silver halide grains in the photomicrograph can be summed separately, and from the two sums the percentage of the total projected area of the silver halide grains provided by the tabular grains meeting the thickness and diameter criteria can be

calculated.

In the above determinations a reference tabular grain thickness of less than 0.3 micron was chosen to distinguish the uniquely thin tabular grains herein contemplated from thicker tabular grains which provide inferior photographic properties. A reference grain diameter of 0.6 micron was chosen, since at lower diameters it is not always possible to distinguish tabular and nontabular grains in micrographs. The term 'projected area' is used in the same sense as the terms 'projection area' and 'projective area' commonly employed in the art; see, for example, James and Higgins, *Fundamentals of Photographic Theory*, Morgan and Morgan, New York, p 15.

In a preferred form offering a broad range of observed advantages the present disclosure employs high aspect ratio silver bromoiodide emulsions. High aspect ratio tabular grain silver bromoiodide emulsions can be prepared by introducing into a conventional reaction vessel for silver halide precipitation equipped with an efficient stirring mechanism dispersing medium. Typically the dispersing medium initially introduced into the reaction vessel is at least about 10 percent by weight based on total weight of the dispersing medium present in the silver bromoiodide emulsion at the conclusion of grain precipitation. Since dispersing medium can be removed from the reaction vessel by ultrafiltration during silver bromoiodide grain precipitation, as taught by Mignot US Patent 4,334,012, here incorporated by reference, it is appreciated that the volume of dispersing medium initially present in the reaction vessel can equal or even exceed the volume of the silver bromoiodide emulsion present in the reaction vessel at the conclusion of grain precipitation. The dispersing medium initially introduced into the reaction vessel is preferably water or a dispersion of peptizer in water, optionally containing other ingredients, such as one or more silver halide ripening agents and/or metal dopants, more specifically described below. Additional dispersing medium is added to the reaction vessel with the silver and halide salts and can also be introduced through a separate jet. It is common practice to adjust the proportion of dispersing medium, particularly to increase the proportion of peptizer, after the completion of the salt introductions.

A minor portion of the bromide salt employed in forming the silver bromoiodide grains is initially present in the reaction vessel to adjust the bromide ion concentration of the dispersing medium at the outset of silver bromoiodide precipitation. Also, the dispersing medium in the reaction vessel is initially substantially free of iodide ions. As employed herein, the term 'substantially free of iodide ions' as applied to the contents of the reaction vessel means that there are insufficient iodide ions present as compared to bromide ions to precipitate as a separate silver iodide phase. It is contemplated to maintain the pBr of the reaction vessel initially in the range of from at or below 1.6 to at or above 0.6. In the absence or diminished presence of a peptizer such as gelatin higher initial pBr levels can be employed. (As herein employed, pBr is defined as the negative logarithm of bromide ion concentration. pH, pCl, pI, and pAg are similarly defined for hydrogen, chloride, iodide, and silver ion concentrations, respectively).

During precipitation silver, bromide, and iodide salts are added to the reaction vessel by techniques well known in the precipitation of silver bromoiodide grains. Typically an aqueous silver salt solution of a soluble silver salt, such as silver nitrate, is introduced into the reaction vessel concurrently with the introduction of the bromide and iodide salts. The bromide and iodide salts are also typically introduced as aqueous salt solutions, such as aqueous solutions of one or more soluble ammonium, alkali metal (eg, sodium or potassium), or alkaline earth metal (eg, magnesium or calcium) halide salts. The silver salt is at least initially introduced into the reaction vessel separately from the iodide salt. The iodide and bromide salts can be added to the reaction vessel separately or as a mixture.

It is possible to increase the permissible latitude of pBr during concurrent introduction of silver, bromide, and iodide salts. Raising pBr values above 2.2 during tabular grain growth results in thickening of the grains, but can be tolerated in many instances while still realizing an average aspect ratio of greater than 8:1.

As an alternative to the introduction of silver, bromide, and iodide salts as aqueous solutions, it is specifically contemplated to introduce the silver, bromide, and iodide salts, initially or in the growth stage, in the form of fine silver halide grains suspended in dispersing medium. The grains are sized so that they are readily Ostwald ripened onto larger grain nuclei, if any are present, once introduced into the reaction vessel. The maximum useful grain sizes will depend on the specific conditions within the reaction vessel, such as temperature and the presence of solubilizing and ripening agents. Silver bromide, silver iodide, and/or silver bromoiodide grains can be introduced. (Since bromide and/or iodide are precipitated in preference to chloride, it is also possible to employ silver chlorobromide and silver chlorobromoiodide grains). The silver halide grains are preferably very fine.

Subject to the pBr requirements set forth above, the concentrations and rates of silver, bromide, and iodide salt introductions can take any convenient conventional form. The silver and halide salts are preferably introduced in concentrations of from 0.1 to 5 moles per liter, although broader conventional concen-

tration ranges, such as from 0.01 mole per liter to saturation, for example, are contemplated. Specifically preferred precipitation techniques are those which achieve shortened precipitation times by increasing the rate of silver and halide salt introduction during the run. The rate of silver and halide salt introduction can be increased either by increasing the rate at which the dispersing medium and the silver and halide salts are introduced or by increasing the concentrations of the silver and halide salts within the dispersing medium being introduced. It is specifically preferred to increase the rate of silver and halide salt introduction, but to maintain the rate of introduction below the threshold level at which the formation of new grain nuclei is favored — ie, to avoid renucleation, as taught by Irie US Patent 3,650,757, Kurz US Patent 3,672,900, Saito US Patent 4,242,445, Wilgus German OLS 2,107,118, Teitscheid et al European Patent Application 80102242, and Wey 'Growth Mechanism of AgBr Crystals in Gelatin Solution', *Photographic Science and Engineering*, Vol 21, No 1, January /February 1977, p 14, *et seq.* By avoiding the formation of additional grain nuclei after passing into the growth stage of precipitation, relatively monodispersed tabular silver bromoiodide grain populations can be obtained. Emulsions having coefficients of variation of less than about 30 percent can be prepared. (As employed herein the coefficient of variation is defined as 100 times the standard deviation of the grain diameter divided by the average grain diameter). By intentionally favoring renucleation during the growth stage of precipitation, it is, of course, possible to produce polydispersed emulsions of substantially higher coefficients of variation. To reduce the coefficient of variation of tabular grains it is preferred to increase pBr, either gradually or abruptly, such as by the gradual or abrupt separate addition of dispersing medium early in the precipitation.

The concentration of iodide in the silver bromoiodide emulsions can be controlled by the introduction of iodide salts. Any conventional iodide concentration can be employed. Even very small amounts of iodide — eg, as low as 0.05 mole percent — are recognized in the art to be beneficial. In their preferred form the emulsions of the present disclosure incorporate at least about 0.1 mole percent iodide. Silver iodide can be incorporated into the tabular silver bromoiodide grains up to its solubility limit in silver bromide at the temperature of grain formation. Thus, silver iodide concentrations of up to about 40 mole percent in the tabular silver bromoiodide grains can be achieved at precipitation temperatures of 90°C. In practice precipitation temperatures can range down to near ambient room temperatures — eg, about 30°C. It is generally known in the art to optimize iodide concentrations for the specific photographic application.

The relative proportion of iodide and bromide salts introduced into the reaction vessel during precipitation can be maintained in a fixed ratio to form a substantially uniform iodide profile in the tabular silver bromoiodide grains or varied, as by increasing the proportion of iodide in annular or otherwise laterally displaced regions of high aspect ratio tabular grains silver bromoiodide emulsions as compared to central regions of the tabular grains. In a variant form it is specifically contemplated to terminate iodide or bromide and iodide salt addition to the reaction vessel prior to the termination of silver salt addition so that excess halide reacts with the silver salt. This results in a shell of silver bromide being formed on the tabular silver bromoiodide grains. Thus, it is apparent that the tabular silver bromoiodide grains of the present disclosure can exhibit substantially uniform or graded iodide concentration profiles and that the gradation can be controlled, as desired, to favor higher iodide concentrations internally or at or near the surfaces of the tabular silver bromoiodide grains.

High aspect ratio tabular grain silver bromide emulsions lacking iodide can be prepared by the process described above modified to exclude iodide. High aspect ratio tabular grains silver bromide emulsions can alternatively be prepared following procedures previously taught in the art.

The tabular grain silver bromide and bromoiodide emulsions of this disclosure typically contain {111} crystal planes. Silver bromide tabular grains which appear square or rectangular in projected area have been prepared by ripening seed grains in the substantial absence of nonhalide silver ion complexing agents in the pAg range of from 5.0 to 8.0. Such tabular grains are believed to be bounded by {100} crystal faces. The tabular grain silver bromide and silver bromoiodide emulsions of this disclosure can contain tabular grains bounded by {100}, {110}, and {111} crystal faces, and the selection of grain crystal faces can be controlled by selection of grain precipitation and growth conditions.

Certain of the advantages achieved in the practice of this disclosure, are independent of the halide content of the high aspect ratio tabular grain emulsions. A process of preparing tabular silver chloride grains which are substantially internally free of both silver bromide and silver iodide employs a double-jet precipitation process wherein chloride and silver salts are concurrently introduced into a reaction vessel containing dispersing medium in the presence of ammonia. During chloride salt introduction the pAg within the dispersing medium is in the range of from 6.5 to 10 and the pH in the range of from 8 to 10. The presence of ammonia at higher temperatures tends to cause thick grains to form, therefore

precipitation temperatures are limited. The process can be optimized to produce high aspect ratio tabular grain silver chloride emulsions.

A process of preparing tabular grains of at least 50 mole percent chloride having opposed crystal faces lying in $\{111\}$ crystal planes and, in one preferred form, at least one peripheral edge lying parallel to a $\langle 211 \rangle$ crystallographic vector in the plane of one of the major surfaces can be practiced by reacting aqueous silver and chloride-containing halide salt solutions in the presence of a crystal habit modifying amount of an amino-substituted azaindene and a peptizer having a thioether linkage.

Tabular grain emulsions wherein the silver halide grains contain chloride and bromide in at least annular grain regions and preferably throughout are contemplated. The tabular grain regions containing silver, chloride, and bromide are formed by maintaining a molar ratio of chloride and bromide ions of from 1.6:1 to about 260:1 and the total concentration of halide ions in the reaction vessel in the range of from 0.10 to 0.90 normal during introduction of silver, chloride, bromide, and, optionally, iodide salts into the reaction vessel. The molar ratio of silver chloride to silver bromide in the tabular grains can range from 1:99 to 2:3.

High aspect ratio tabular grain emulsions useful in the practice of this disclosure can have extremely high average aspect ratios. Tabular grain average aspect ratios can be increased by increasing average grain diameters. This can produce sharpness advantages, but maximum average grain diameters are generally limited by granularity requirements for a specific photographic application. Tabular grain average aspect ratios can also or alternatively be increased by decreasing average grain thicknesses. When silver coverages are held constant, decreasing the thickness of tabular grains generally improves granularity as a direct function of increasing aspect ratio. Hence the maximum average aspect ratios of the tabular grain emulsions of this disclosure are a function of the maximum average grain diameters acceptable for the specific photographic application and the minimum attainable tabular grain thicknesses which can be produced. Maximum average aspect ratios have been observed to vary, depending upon the precipitation technique employed and the tabular grain halide composition. The highest observed average aspect ratios, 500:1, for tabular grains with photographically useful average grain diameters, have been achieved by Ostwald ripening preparations of silver bromide grains, with aspect ratios of 100:1, 200:1, or even higher being obtainable by double-jet precipitation procedures. The presence of iodide generally decreases the maximum average aspect ratios realized, but the preparation of silver bromoiodide tabular grain emulsions having average aspect ratios of 100:1 or even 200:1 or more is feasible. Average aspect ratios as high as 50:1 or even 100:1 for silver chloride tabular grains, optionally containing bromide and/or iodide, can be prepared as taught above.

Modifying compounds can be present during tabular grain precipitation. Such compounds can be initially in the reaction vessel or can be added along with one or more of the salts according to conventional procedures. Modifying compounds, such as compounds of copper, thallium, lead, bismuth, cadmium, zinc, middle chalcogens (ie, sulfur, selenium, and tellurium), gold, and Group VIII noble metals, can be present during silver halide precipitation, as illustrated by Arnold et al US Patent 1,195,432, Hochstetter US Patent 1,951,933, Trivelli et al US Patent 2,448,060, Overman US Patent 2,628,167, Mueller et al US Patent 2,950,972, Sidebotham US Patent 3,488,709, Rosecrants et al US Patent 3,737,313, Berry et al US Patent 3,772,031, Atwell US Patent No 4,269,927, and *Research Disclosure*, Vol 134, June 1975, Item 13452. *Research Disclosure* and its predecessor, *Product Licensing Index*, are publications of Industrial Opportunities Ltd; Homewell, Havant, Hampshire, PO9 1EF, United Kingdom. The tabular grain emulsions can be internally reduction sensitized during precipitation, as illustrated by Moir et al, *Journal of Photographic Science*, Vol 25, 1977, pp 19-27.

The individual silver and halide salts can be added to the reaction vessel through surface or subsurface delivery tubes by gravity feed or by delivery apparatus for maintaining control of the rate of delivery and the pH, pBr, and/or pAg of the reaction vessel contents, as illustrated by Culhane et al US Patent 3,821,002, Oliver US Patent 3,031,304 and Claes et al, *Photographische Korrespondenz*, 102 Band, Number 10, 1967, p 162. In order to obtain rapid distribution of the reactants within the reaction vessel, specially constructed mixing devices can be employed, as illustrated by Audran US Patent 2,996,287, McCrossen et al US Patent 3,342,605, Frame et al US Patent 3,415,650, Porter et al US Patent 3,785,777, Finnicum et al US Patent 4,147,551, Verhille et al US Patent 4,171,224, Calamur UK Patent Application 2,022,431A, Saito et al German OLS 2,555,364, and 2,556,885, and *Research Disclosure*, Volume 166, February 1978, Item 16662.

In forming the tabular grain emulsions peptizer concentrations of up to about 10 percent by weight, based on the total weight of emulsion components in the reaction vessel, can be conveniently employed. It is common practice to maintain the concentration of the peptizer in the reaction vessel well of below 10 percent, based on the total weight, prior to and during silver halide formation and to adjust the emulsion vehicle concentration upwardly for optimum

coating characteristics by delayed, supplemental vehicle additions. It is contemplated that the emulsion as initially formed will contain from about 5 to 50 grams of peptizer per mole of silver halide. Additional vehicle can be added later to bring the concentration up to as high as 1000 grams per mole of silver halide.

Vehicles (which include both binders and peptizers) can be chosen from among those conventionally employed in silver halide emulsions. Preferred peptizers are hydrophilic colloids, which can be employed alone or in combination with hydrophobic materials. Suitable hydrophilic materials include substances such as proteins, protein derivatives, cellulose derivatives — eg, cellulose esters, gelatin — eg, alkali treated gelatin (cattle bone or hide gelatin) or acid-treated gelatin (pigskin gelatin), gelatin derivatives — eg, acetylated gelatin, phthalated gelatin and the like, polysaccharides such as dextran, gum arabic, zein, casein, pectin, collagen derivatives, agar-agar, arrowroot, albumin and the like as described in Yutzy et al US patents 2,614,928 and '929, Lowe et al US Patents 2,691,582, 2,614,930, '931, 2,327,808 and 2,448,534, Gates et al US Patents 2,787,545 and 2,956,880, Himmelmann et al US Patent 3,061,436, Farrel et al US Patent 2,816,027, Ryan US Patents 3,132,945, 3,138,461 and 3,186,846, Dersh et al UK Patent 1,167,159 and US Patents 2,960,405 and 3,436,220, Geary US Patent 3,486,896, Gazzard UK Patent 793,549, Gates et al US Patents 2,992,213, 3,157,506, 3,184,312 and 3,539,353, Miller et al US Patent 3,227,571, Boyer et al US Patent 3,532,502, Malan et al US Patent 3,551,151, Lohmer et al US Patent 4,018,609, Luciani et al UK Patent 1,186,790, Hori et al UK Patent 1,489,080 and Belgian Patent 856,631, UK Patent 1,490,644, UK Patent 1,483,551, Arase et al UK Patent 1,459,906, Salo US Patents 2,110,491 and 2,311,086, Fallesen US Patent 2,343,650, Yutzy US Patent 2,322,085, Lowe US Patent 2,563,791, Talbot et al US Patent 2,725,293, Hilborn US Patent 2,748,022, DePauw et al US Patent 2,956,883, Ritchie UK Patent 2,095, DeStubner US Patent 1,752,069, Sheppard et al US Patent 2,127,573, Lieng US Patent 2,256,720, Gaspar US Patent 2,361,936, Farmer UK Patent 15,727, Stevens UK Patent 1,062,116 and Yamamoto et al US Patent 3,923,517.

Other materials commonly employed in combination with hydrophilic colloid peptizers as vehicles (including vehicle extenders — eg, materials in the form of latices) include synthetic polymeric peptizers, carriers and/or binders such as poly(vinyl lactams), acrylamide polymers, polyvinyl alcohol and its derivatives, polyvinyl acetals, polymers of alkyl and sulfoalkyl acrylates and methacrylates, hydrolyzed polyvinyl acetates, polyamides, polyvinyl pyridine, acrylic acid polymers, maleic anhydride copolymers, polyalkylene oxides, methacrylamide copolymers, polyvinyl oxazolidinones, maleic acid copolymers, vinylamine copolymers, methacrylic acid copolymers, acryloyloxyalkylsulfonic acid copolymers, sulfoalkylacrylamide copolymers, polyalkyleneimine copolymers, polyamines, N,N-dialkylaminoalkyl acrylates, vinyl imidazole copolymers, vinyl sulfide copolymers, halogenated styrene polymers, amineacrylamide polymers, polyepoxides and the like as described in Hollister et al US Patents 3,679,425, 3,706,564 and 3,813,251, Lowe US Patents 2,253,078, 2,276,322, '323, 2,281,703, 2,311,058 and 2,414,207, Lowe et al US Patents 2,484,456, 2,541,474 and 2,632,704, Perry et al US Patent 3,425,836, Smith et al US Patents 3,415,653 and 3,615,624, Smith US Patent 3,488,708, Whiteley et al US Patents 3,392,025 and 3,511,818, Fitzgerald US Patents 3,681,079, 3,721,565, 3,852,073, 3,861,918 and 3,925,083, Fitzgerald et al US Patent 3,879,205, Nottorf US Patent 3,142,568, Houck et al US Patents 3,062,674 and 3,220,844, Dann et al US Patent 2,882,161, Schupp US Patent 2,579,016, Weaver US Patent 2,829,053, Alles et al US Patent 2,698,240, Priest et al US Patent 3,003,879, Merrill et al US Patent 3,419,397, Stonham US Patent 3,284,207, Lohmer et al US Patent 3,167,430, Williams US Patent 2,957,767, Dawson et al US Patent 2,893,867, Smith et al US Patents 2,860,986 and 2,904,539, Ponticello et al US Patents 3,929,482 and 3,860,428, Ponticello US Patent 3,939,130, Dykstra US Patent 3,411,911 and Dykstra et al Canadian Patent 774,054, Ream et al US Patent 3,287,289, Smith UK Patent 1,466,600, Stevens UK Patent 1,062,116, Fordyce US Patent 2,211,323, Martinez US Patent 2,284,877, Watkins US Patent 2,420,455, Jones US Patent 2,533,166, Bolton US Patent 2,495,918, Graves US Patent 2,289,775, Yackel US Patent 2,565,418, Unruh et al US Patents 2,865,893 and 2,875,059, Rees et al US Patent 3,536,491, Broadhead et al UK Patent 1,348,815, Taylor et al US Patent 3,479,186, Merrill et al US Patent 3,520,857, Bacon et al US Patent 3,690,888, Bowman US Patent 3,748,143, Dickinson et al UK Patents 808,227 and '228, Wood UK Patent 822,192 and Iguchi et al UK Patent 1,398,055. These additional materials need not be present in the reaction vessel during silver halide precipitation, but rather are conventionally added to the emulsion prior to coating. The vehicle materials, including particularly the hydrophilic colloids, as well as the hydrophobic materials useful in combination therewith can be employed not only in the emulsion layers of the photographic elements of this disclosure, but also in other layers, such as overcoat layers, interlayers and layers positioned beneath the emulsion layers.

It is specifically contemplated that grain ripening can occur during the preparation of silver halide emulsions according to the

present disclosure. Known silver halide solvents are useful in promoting ripening. For example, an excess of bromide ions, when present in the reaction vessel, is known to promote ripening. It is therefore apparent that the bromide salt solution run into the reaction vessel can itself promote ripening. Other ripening agents can also be employed and can be entirely contained within the dispersing medium in the reaction vessel before silver and halide salt addition, or they can be introduced into the reaction vessel along with one or more of the halide salt, silver salt, or peptizer. In still another variant the ripening agent can be introduced independently during halide and silver salt additions. Illustrative prior teachings of employing thiocyanate ripening agents are found in Nietz et al, US Patent 2,222,264, cited above; Lowe et al US Patent 2,448,534 and Illingsworth US Patent 3,320,069. Alternatively, conventional thioether ripening agents, such as those disclosed in McBride US Patent 3,271,157, Jones US Patent 3,574,628, and Rosecrants et al US Patent 3,737,313 can be employed.

The high aspect ratio tabular grain emulsions of the present disclosure are preferably washed to remove soluble salts. The soluble salts can be removed by decantation, filtration, and/or chill setting and leaching, as illustrated by Craft US Patent 2,316,845 and McFall et al US Patent 3,396,027; by coagulation washing, as illustrated by Hewitson et al US Patent 2,618,556, Yutzy et al US Patent 2,614,928, Yackel US Patent 2,565,418, Hart et al US Patent 3,241,969, Waller et al US Patent 2,489,341, Klinger UK Patent 1,305,409 and Dersch et al UK Patent 1,167,159; by centrifugation and decantation of a coagulated emulsion, as illustrated by Murray US Patent 2,463,794, Ujihara et al US Patent 3,707,378, Audran US Patent 2,996,287 and Timson US Patent 3,498,454; by employing hydrocyclones alone or in combination with centrifuges, as illustrated by UK Patent 1,336,692, Claes UK Patent 1,356,573 and Ushomirskii et al *Soviet Chemical Industry*, Vol 6, No 3, 1974, pp 181-185; by diafiltration with a semipermeable membrane, as illustrated by *Research Disclosure*, Vol 102, October 1972, Item 10208, Hagemair et al *Research Disclosure*, Vol 131, March 1975, Item 13122, Bonnet *Research Disclosure*, Vol 135, July 1975, Item 13577, Berg et al German OLS 2,436,461, Bolton US Patent 2,495,918, and Mignot US Patent 4,334,012 cited above, or by employing an ion exchange resin, as illustrated by Maley US Patent 3,782,953 and Noble US Patent 2,827,428. The emulsions, with or without sensitizers, can be dried and stored prior to use as illustrated by *Research Disclosure*, Vol 101, September 1972, Item 10152. In the present disclosure washing is particularly advantageous in terminating ripening of the tabular grains after the completion of precipitation to avoid increasing their thickness and reducing their aspect ratio.

Once the high aspect ratio tabular grain emulsions have been formed they can be shelled to produce core-shell emulsions by procedures well known to those skilled in the art. Any photographically useful silver salt can be employed in forming shells on the high aspect ratio tabular grain emulsions prepared by the present process. Techniques for forming silver salt shells are illustrated by Berriman US Patent 3,367,778, Porter et al US Patents 3,206,313 and 3,317,322, Morgan US Patent 3,917,485, and Maternaghan, US Patents 4,184,877 and '878. Since conventional techniques for shelling do not favor the formation of high aspect ratio tabular grains, as shell growth proceeds the average aspect ratio of the emulsion declines. If conditions favorable for tabular grain formation are present in the reaction vessel during shell formation, shell growth can occur preferentially on the outer edges of the grains so that aspect ratio need not decline. Shelling tabular grains without necessarily reducing the aspect ratios of the resulting core-shell grains as compared to the tabular grains employed as core grains is specifically contemplated.

Although the procedures for preparing tabular silver halide grains described above will produce high aspect ratio tabular grain emulsions in which tabular grains satisfying the thickness and diameter criteria for aspect ratio account for at least 50 percent of the total projected area of the total silver halide grain population, it is recognized that further advantages can be realized by increasing the proportion of such tabular grains present. Preferably at least 70 percent (optimally at least 90 percent) of the total projected area is provided by tabular silver halide grains meeting the thickness and diameter criteria. While minor amounts of non-tabular grains are fully compatible with many photographic applications, to achieve the full advantages of tabular grains the proportion of tabular grains can be increased. Larger tabular silver halide grains can be mechanically separated from smaller, nontabular grains in a mixed population of grains using conventional separation techniques — eg, by using a centrifuge or hydrocyclone. An illustrative teaching of hydrocyclone separation is provided by Audran et al US Patent 3,326,641.

The high aspect ratio tabular grain silver halide emulsions of the present disclosure can be chemically sensitized. These and other silver halide emulsions herein disclosed can be chemically sensitized with active gelatin, as illustrated by T H James, *The Theory of the*

Photographic Process, 4th Ed, Macmillan, 1977, pp 67-76, or with sulfur, selenium, tellurium, gold, platinum, palladium, iridium, osmium, rhodium, rhenium, or phosphorus sensitizers or combinations of these sensitizers, such as at pAg levels of from 5 to 10, pH levels of from 5 to 8 and temperatures of from 30 to 80°C, as illustrated by *Research Disclosure*, Vol 120, April 1974, Item 12008, *Research Disclosure*, Vol 134, June 1975, Item 13452, Sheppard et al US Patent 1,623,499, Matties et al US Patent 1,673,522, Waller et al US Patent 2,399,083, Damschroder et al US Patent 2,642,361, McVeigh US Patent 3,297,447, Dunn US Patent 3,297,446, McBride UK Patent 1,315,755, Berry et al US Patent 3,772,031, Gilman et al US Patent 3,761,267, Ohi et al US Patent 3,857,711, Klinger et al US Patent 3,565,633, Oftedahl US Patents 3,901,714 and 3,904,415 and Simons UK Patent 1,396,696; chemical sensitization being optionally conducted in the presence of thiocyanate compounds, as described in Damschroder US Patent 2,642,361; sulfur containing compounds of the type disclosed in Lowe et al US Patent 2,521,926, Williams et al US Patent 3,021,215, and Bigelow US Patent 4,054,457. It is specifically contemplated to sensitize chemically in the presence of finish (chemical sensitization) modifiers — that is, compounds known to suppress fog and increase speed when present during chemical sensitization, such as azaindenes, azapyridazines, azapyrimidines, benzothiazolium salts, and sensitizers having one or more heterocyclic nuclei. Exemplary finish modifiers are described in Brooker et al US Patent 2,131,038, Dostes US Patent 3,411,914, Kuwabara et al US Patent 3,554,757, Oguchi et al US Patent 3,565,631, Oftedahl US Patent 3,901,714, Walworth Canadian Patent 778,723, and Duffin *Photographic Emulsion Chemistry*, Focal Press (1966), New York, pp 138-143. Additionally or alternatively, the emulsions can be reduction sensitized — eg, with hydrogen, as illustrated by Janusonis US Patent 3,891,446 and Babcock et al US Patent 3,984,249, by low pAg (eg, less than 5) and/or high pH (eg, greater than 8) treatment or through the use of reducing agents, such as stannous chloride, thiourea dioxide, polyamines and amineboranes, as illustrated by Allen et al US Patent 2,983,609, Oftedahl et al *Research Disclosure*, Vol 136, August 1975, Item 13654, Lowe et al US Patents 2,518,698 and 2,739,060, Roberts et al US Patents 2,743,182 and '183, Chambers et al US Patent 3,026,203 and Bigelow et al US Patent 3,361,564. Surface chemical sensitization, including sub-surface sensitization, illustrated by Morgan US Patent 3,917,485 and Becker US Patent 3,966,476, is specifically contemplated.

In addition to being chemically sensitized the high aspect ratio tabular grain silver halide emulsions of the present disclosure can also be spectrally sensitized. It is specifically contemplated to employ in combination with the high aspect ratio tabular grain emulsions and other emulsions disclosed herein spectral sensitizing dyes that exhibit absorption maxima in the blue and minus blue — ie, green and red, portions of the visible spectrum. In addition, for specialized applications, spectral sensitizing dyes can be employed which improve spectral response beyond the visible spectrum. For example, the use of infrared absorbing spectral sensitizers is specifically contemplated.

The silver halide emulsions of this disclosure can be spectrally sensitized with dyes from a variety of classes, including the polymethine dye class, which classes include the cyanines, merocyanines, complex cyanines and merocyanines (ie, tri-, tetra-, and poly-nuclear cyanines and merocyanines), oxonols, hemioxonols, styryls, merostyryls, and streptocyanines.

The cyanine spectral sensitizing dyes include, joined by a methine linkage, two basic heterocyclic nuclei, such as those derived from quinolinium, pyridinium, isoquinolinium, 3H-indolium, benz[e]indolium, oxazolium, oxazolinium, thiazolium, thiazolinium, selenazolium, selenazolinium, imidazolium, imidazolinium, benzoxazolium, benzothiazolium, benzoselenazolium, benzimidazolium, naphthoxazolium, naphthothiazolium, naphthoselenazolium, dihydronaphthothiazolium, pyrylium, and imidazopyrazinium quaternary salts.

The merocyanine spectral sensitizing dyes include, joined by a double bond or a methine linkage, a basic heterocyclic nucleus of the cyanine dye type and an acidic nucleus, such as can be derived from barbituric acid, 2-thiobarbituric acid, rhodanine, hydantoin, 2-thiohydantoin, 4-thiohydantoin, 2-pyrazolin-5-one, 2-isoxazolin-5-one, indan-1,3-dione, cyclohexane-1,3-dione, 1,3-dioxane-4,6-dione, pyrazolin-3,5-dione, pentane-2,4-dione, alkylsulfonylacetonitrile, malononitrile, isoquinolin-4-one, and chroman-2,4-dione.

One or more spectral sensitizing dyes may be used. Dyes with sensitizing maxima at wavelengths throughout the visible spectrum and with a great variety of spectral sensitivity curve shapes are known. The choice and relative proportions of dyes depend upon the region of the spectrum to which sensitivity is desired and upon the shape of the spectral sensitivity curve desired. Dyes with overlapping spectral sensitivity curves will often yield in combination a curve in which the sensitivity at each wavelength in the area of overlap is approximately equal to the sum of the sensitivities of the individual dyes. Thus, it is possible to use combinations of dyes with different maxima to achieve a spectral sensitivity curve with a maximum intermediate to the sensitizing maxima of the individual dyes.

Combinations of spectral sensitizing dyes can be used which result in supersensitization — that is, spectral sensitization that is greater in some spectral region than that from any concentration of one of the dyes alone or that which would result from the additive effect of the dyes. Supersensitization can be achieved with selected combinations of spectral sensitizing dyes and other addenda, such as stabilizers and antifoggants, development accelerators or inhibitors, coating aids, brighteners and antistatic agents. Any one of several mechanisms as well as compounds which can be responsible for supersensitization are discussed by Gilman, 'Review of the Mechanisms of Supersensitization', *Photographic Science and Engineering*, Vol 18, 1974, pp 418-430.

Spectral sensitizing dyes also affect the emulsions in other ways. Spectral sensitizing dyes can also function as antifoggants or stabilizers, development accelerators or inhibitors, and halogen acceptors or electron acceptors, as disclosed in Brooker et al US Patent 2,131,038 and Shiba et al US Patent 3,930,860.

Sensitizing action can be correlated to the position of molecular energy levels of a dye with respect to ground state and conduction band energy levels of the silver halide crystals. These energy levels can in turn be correlated to polarographic oxidation and reduction potentials, as discussed in *Photographic Science and Engineering*, Vol 18, 1974, pp 49-53 (Sturmer et al), pp 175-178 (Leubner) and pp 475-485 (Gilman). Oxidation and reduction potentials can be measured as described by R F Large in *Photographic Sensitivity*, Academic Press, 1973, Chapter 15.

The chemistry of cyanine and related dyes is illustrated by Weissberger and Taylor, *Special Topics of Heterocyclic Chemistry*, John Wiley and Sons, New York, 1977, Chapter VIII; Venkataraman, *The Chemistry of Synthetic Dyes*, Academic Press, New York, 1971, Chapter V; James, *The Theory of the Photographic Process*, 4th Ed, Macmillan, 1977, Chapter 8, and F M Hamer, *Cyanine Dyes and Related Compounds*, John Wiley and Sons, 1964.

Among useful spectral sensitizing dyes for sensitizing silver halide emulsions are those found in UK Patent 742,112, Brooker US Patents 1,846,300, '301, '302, '303, '304, 2,078,233 and 2,089,729, Brooker et al US Patents 2,165,338, 2,213,238, 2,231,658, 2,493,747, '748, 2,526,632, 2,739,964 (Reissue 24,292), 2,778,823, 2,917,516, 3,352,857, 3,411,916 and 3,431,111, Wilmanns et al US Patent 2,295,276 Sprague US Patents 2,481,698 and 2,503,776, Carroll et al US Patents 2,688,545 and 2,704,714, Larive et al US Patent 2,921,067, Jones US Patent 2,945,763, Nys et al US Patent 3,282,933, Schwan et al US Patent 3,397,060, Riester US Patent 3,660,102, Kampfer et al US Patent 3,660,103, Taber et al US Patents 3,335,010, 3,352,680 and 3,384,486, Lincoln et al US Patent 3,397,981, Fumia et al US Patents 3,482,978 and 3,623,881, Spence et al US Patent 3,718,470 and Mee US Patent 4,025,349. Examples of useful dye combinations, including supersensitizing dye combinations, are found in Motter US Patent 3,506,443 and Schwan et al US Patent 3,672,898. As examples of supersensitizing combinations of spectral sensitizing dyes and non-light absorbing addenda, it is specifically contemplated to employ thiocyanates during spectral sensitization, as taught by Leermakers US Patent 2,221,805; bis-triazinylaminostilbenes, as taught by McFall et al US Patent 2,933,390; sulfonated aromatic compounds, as taught by Jones et al US Patent 2,937,089; mercapto-substituted heterocycles, as taught by Riester US Patent 3,457,078; iodide, as taught by UK Patent 1,413,826; and still other compounds, such as those disclosed by Gilman, 'Review of the Mechanisms of Supersensitization', cited above.

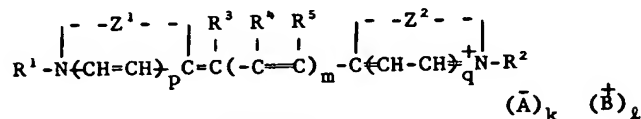
Conventional amounts of dyes can be employed in spectrally sensitizing the emulsion layers containing nontabular or low aspect ratio tabular silver halide grains. To realize the full advantages of this disclosure it is preferred to adsorb spectral sensitizing dye to the grain surfaces of the high aspect ratio tabular grain emulsions in a substantially optimum amount — that is, in an amount sufficient to realize at least 60 percent of the maximum photographic speed attainable from the grains under contemplated conditions of exposure. The quantity of dye employed will vary with the specific dye or dye combination chosen as well as the size and aspect ratio of the grains. It is known in the photographic art that optimum spectral sensitization is obtained with organic dyes at about 25 to 100 percent or more of monolayer coverage of the total available surface area of surface sensitive silver halide grains, as disclosed, for example, in West et al, 'The Adsorption of Sensitizing Dyes in Photographic Emulsions', *Journal of Phys Chem*, Vol 56, p 1065, 1952; Spence et al, 'Desensitization of Sensitizing Dyes', *Journal of Physical and Colloid Chemistry*, Vol 56, No 6, June 1948, pp 1090-1103; and Gilman et al US Patent 3,979,213. Optimum dye concentration levels can be chosen by procedures taught by Mee, *Theory of the Photographic Process*, pp 1067-1069, cited above.

Although native blue sensitivity of silver bromide or bromoiodide is usually relied upon in the art in emulsion layers intended to record exposure to blue light, it is a specific feature of the present disclosure that significant advantages can be obtained by the use of spectral sensitizers, even where their principal absorption is in the spectral region to which the emulsions possess native sensitivity. For example, it is specifically recognized that advantages can be realized from the use of blue spectral sensitizing dyes. Even when

the emulsions of the disclosure are high aspect ratio tabular grain silver bromide and silver bromoiodide emulsions, very large increases in speed are realized by the use of blue spectral sensitizing dyes. Where it is intended to expose emulsions according to the present disclosure in their region of native sensitivity, advantages in sensitivity can be gained by increasing the thickness of the tabular grains. In one preferred form of the disclosure the emulsions are blue sensitized silver bromide and bromoiodide emulsions in which the tabular grains having a thickness of less than 0.5 micron and a diameter of at least 0.6 micron have an average aspect ratio of greater than 8:1, preferably at least 12:1 and account for at least 50 percent of the total projected area of the silver halide grains present in the emulsion, preferably 70 percent and optimally at least 90 percent. In the foregoing description 0.3 micron can, of course, be substituted for 0.5 micron without departing from the disclosure.

Useful blue spectral sensitizing dyes for high aspect ratio tabular grain silver bromide and silver bromoiodide emulsions can be selected from any of the dye classes known to yield spectral sensitizers. Polymethine dyes, such as cyanines, merocyanines, hemicyanines, hemioxonols, and merostyryls, are preferred blue spectral sensitizers. Generally useful blue spectral sensitizers can be selected from among these dye classes by their absorption characteristics — ie, hue. There are, however, general structural correlations that can serve as a guide in selecting useful blue sensitizers. Generally the shorter the methine chain, the shorter the wavelength of the sensitizing maximum. Nuclei also influence absorption. The addition of fused rings to nuclei tends to favor longer wavelengths of absorption. Substituents can also alter absorption characteristics. In the formulae which follow, unless otherwise specified, alkyl groups and moieties contain from 1 to 20 carbon atoms, preferably from 1 to 8 carbon atoms. Aryl groups and moieties contain from 6 to 15 carbon atoms and are preferably phenyl or naphthyl groups or moieties.

Preferred cyanine blue spectral sensitizers are monomethine cyanines; however, useful cyanine blue spectral sensitizers can be selected from among those of Formula 1.



Formula 1

where

Z¹ and Z² may be the same or different and each represents the elements needed to complete a cyclic nucleus derived from basic heterocyclic nitrogen compounds such as oxazoline, oxazole, benzoxazole, the naphthoxazoles (eg, naphth[2,1-d]oxazole, naphth[2,3-d]oxazole, and naphth[1,2-d]oxazole), thiazoline, thiazole, benzothiazole, the naphthothiazoles (eg, naphth[2,1-d]thiazole), the thiazoloquinolines (eg, thiazolo[4,5-b]quinoline), selenazoline, selenazole, benzoselenazole, the naphthoselenazoles (eg, naphtho[1,2-d]selenazole), 3H-indole (eg, 3,3-dimethyl-3H-indole), the benzindoles (eg, 1,1-dimethylben[e]indole), imidazoline, imidazole, benzimidazole, the naphthimidazoles (eg, naphth[2,3-d]imidazole), pyridine, and quinoline, which nuclei may be substituted on the ring by one or more of a wide variety of substituents such as hydroxy, the halogens (eg, fluoro, chloro, bromo, and iodo), alkyl groups or substituted alkyl groups (eg, methyl, ethyl, propyl, isopropyl, butyl, octyl, dodecyl, octadecyl, 2-hydroxyethyl, 3-sulfopropyl, carboxymethyl, 2-cyanoethyl, and trifluoromethyl), aryl groups or substituted aryl groups (eg phenyl, 1-naphthyl, 2-naphthyl, 4-sulfophenyl, 3-carboxyphenyl, and 4-biphenyl), aralkyl groups (eg, benzyl and phenethyl), alkoxy groups (eg, methoxy, ethoxy, and isopropoxy), aryloxy groups (eg, phenoxy and 1-naphthoxy), alkylthio groups (eg, methylthio and ethylthio), arylthio groups (eg, phenylthio, p-tolylthio, and 2-naphthylthio), methylenedioxy, cyano, 2-thienyl, styryl, amino or substituted amino groups (eg, anilino, dimethylamino, diethylamino, and morpholino), acyl groups, such as carboxy (eg, acetyl and benzoyl) and sulfo;

R¹ and R² can be the same or different and represent alkyl groups, aryl groups, alkenyl groups, or aralkyl groups, with or without substituents, (eg, carboxymethyl, 2-hydroxyethyl, 3-sulfopropyl, 3-sulfobutyl, 4-sulfobutyl, 4-sulfophenyl, 2-methoxyethyl, 2-sulfatoethyl, 3-thiosulfatopropyl, 2-phosphonoethyl, chlorophenyl, and bromophenyl);

R³ represents hydrogen;

R⁴ and R⁵ represents hydrogen or alkyl of from 1 to 4 carbon atoms;

p and q are 0 or 1, except that both p and q preferably are not 1;

m is 0 or 1 except that when m is 1 both p and q are 0 and at least one of Z¹ and Z² represents imidazoline, oxazoline, thiazoline, or selenazoline;

A is an anionic group;

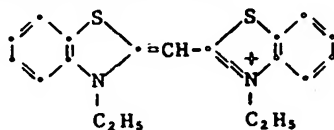
B is a cationic group; and

k and l may be 0 or 1, depending on whether ionic substituents are present. Variants are, of course, possible in which R¹ and R³, R² and R⁵, or R¹ and R² (particularly when m, p, and q are 0) together represent the atoms necessary to complete an alkylene bridge.

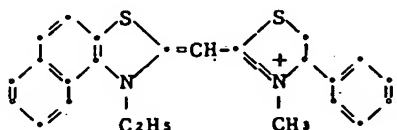
Some representative cyanine dyes useful as blue sensitizers are listed in Table I.

Table I

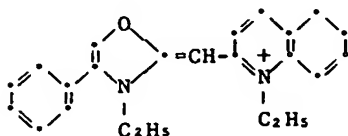
1 3,3'-Diethylthiacyanine bromide



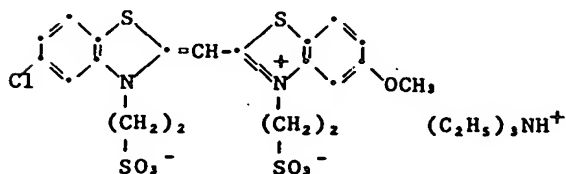
2 1-Ethyl-3' methyl-4'-phenylnaphtho [1,2-d] thiazolothiazolinocyanine bromide



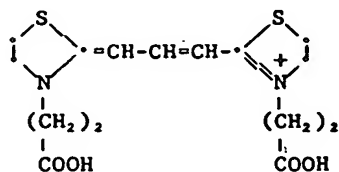
3 1',3-Diethyl-4-phenyloxazolo-2'-cyanine iodide



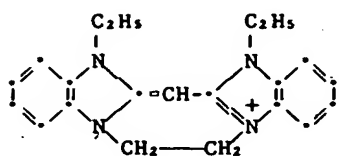
4 Anhydro 5-chloro-5'-methoxy-3,3'-bis-(2-sulfoethyl)-thiacyanine hydroxide, triethylamine salt



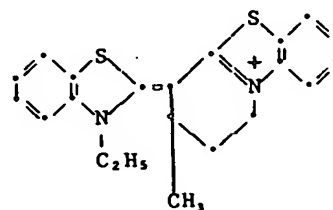
5 3,3'-Bis(2-carboxyethyl)thiazolino-carbocyanine iodide



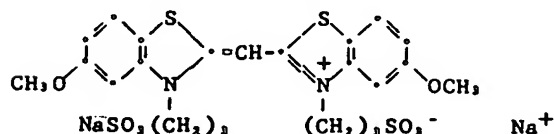
6 1,1'-Diethyl-3,3'-ethylenbenzimidazolocyanine iodide



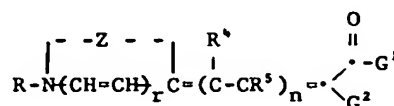
7 1-(3-Ethyl-2-benzothiazolinyldene)-1,2,3,4-tetrahydro-2-methylpyrido-[2,1-b]-benzothiazolinium iodide



8 Anhydro-5, 5'-dimethoxy-3,3'-bis (3-sulfopropyl)-thiacyanine hydroxide; sodium salt



Preferred merocyanine blue spectral sensitizers are zero methine merocyanines; however, useful merocyanine blue spectral sensitizers can be selected from among those of Formula 2.



Formula 2

where

Z represents the same elements as either Z¹ or Z² of Formula 1 above;

R represents the same groups as either R¹ or R² of Formula 1 above;

R⁴ and R⁵ represent hydrogen, an alkyl group of 1 to 4 carbon atoms, or an aryl group (eg, phenyl or naphthyl);

G¹ represents an alkyl group or substituted alkyl group, an aryl or substituted aryl group, an aralkyl group, an alkoxy group, an aryloxy group, a hydroxy group, an amino group, a substituted amino group wherein specific groups are of the types in Formula 1;

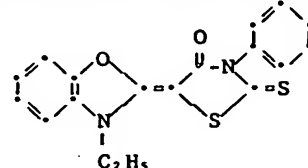
G² can represent any one of the groups listed for G¹ and in addition can represent a cyano group, an alkyl, or arylsulfonyl group, or a group represented by -C-G¹, or G² taken together with

G¹ can represent the elements needed to complete a cyclic acidic nucleus such as those derived from 2,4-oxazolidinone (eg, 3-ethyl-2,4-oxazolidindione), 2,4-thiazolidindione (eg, 3-methyl-2,4-thiazolidindione), 2-thio-2,4-oxazolidindione (eg, 3-phenyl-2-thio-2,4-oxazolidindione), rhodanine, such as 3-ethylrhodanine, 3-phenylrhodanine, 3-(3-dimethylaminopropyl)-rhodanine, and 3-carboxymethylrhodanine, hydantoin (eg, 1,3-diethylhydantoin and 3-ethyl-1-phenylhydantoin), 2-thiohydantoin (eg, 1-ethyl-3-phenyl-2-thiohydantoin, 3-heptyl-1-phenyl-2-thiohydantoin, and 1,3-diphenyl-2-thiohydantoin), 2-pyrazolin-5-one, such as 3-methyl-1-phenyl-2-pyrazolin-5-one, 3-methyl-1-(4-carboxybutyl)-2-pyrazolin-5-one, and 3-methyl-2-(4-sulfophenyl)-2-pyrazolin-5-one, 2-isoxazolin-5-one (eg, 3-phenyl-2-isoxazolin-5-one), 3,5-pyrazolidindione (eg, 1,2-diethyl-3,5-pyrazolidindione and 1,2-diphenyl-3,5-pyrazolidindione), 1,3-indandione, 1,3-dioxane-4,6-dione, 1,3-cyclohexanedione, barbituric acid (eg, 1-ethylbarbituric acid and 1,3-diethylbarbituric acid), and 2-thiobarbituric acid (eg, 1,3-diethyl-2-thiobarbituric acid and 1,3-bis(2-methoxyethyl)-2-thiobarbituric acid);

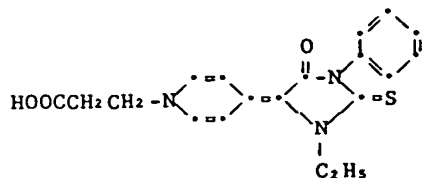
r and n each can be 0 or 1 except that when n is 1 then generally either Z is restricted to imidazoline, oxazoline, selenazoline, thiazoline, imidazole, oxazole, or benzoxazole, or G¹ and G² do not represent a cyclic system. Some representative blue sensitizing merocyanine dyes are listed below in Table II

Table II

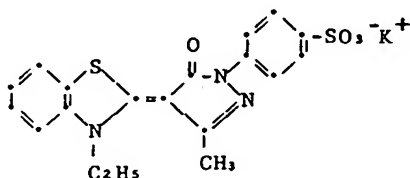
1 5-(3-Ethyl-2-benzoxazolinyldene)-3-phenylrhodanine



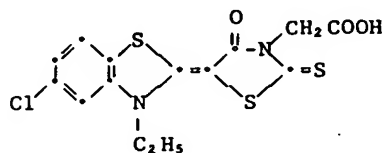
- 2 5-[1-(2-Carboxyethyl)-1,4-dihydro-4-pyridinylidene-1-ethyl-3-phenyl-2-thiohydantoin



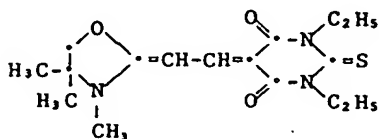
- 3 4-(3-Ethyl-2-benzothiazolinyldiene)-3-methyl-1-(4-sulphophenyl)-2-pyrazolin-5-one, Potassium Salt



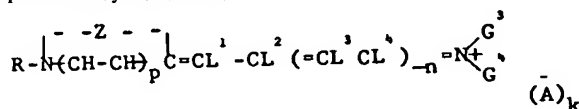
- 4 3-Carboxymethyl-5-(5-chloro-3-ethyl-2-benzothiazolinyldiene)-rhodanine



- 5 1,3-Diethyl-5-[3,4,4-trimethyloxazolidinyldiene]ethylidene]-2-thiobarbituric acid



Useful blue sensitizing hemicyanine dyes include those represented by Formula 3.



Formula 3

where

Z, R, and p represent the same elements as in Formula 2; G³ and G⁴ may be the same or different and may represent alkyl, substituted alkyl, aryl, substituted aryl, or aralkyl, as illustrated for ring substituents in Formula 1 or G³ and G⁴ taken together complete a ring system derived from a cyclic secondary amine, such as pyrrolidine, 3-pyrrolidine, piperidine, piperazine (eg, 4-methylpiperazine and 4-phenylpiperazine), morpholine, 1,2,3,4-tetrahydroquinoline, decahydroquinoline, 3-azabicyclo[3,2,2]nonane, indoline, azetidine, and hexahydroazepine;

L¹ to L⁴ represent hydrogen, alkyl of 1 to 4 carbons, aryl, substituted aryl, or any two of L¹, L², L³, L⁴ can represent the elements needed to complete an alkylene or carbocyclic bridge;

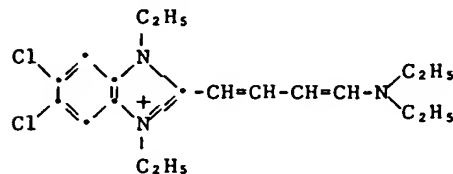
n is 0 or 1; and

A and k have the same definition as in Formula 1.

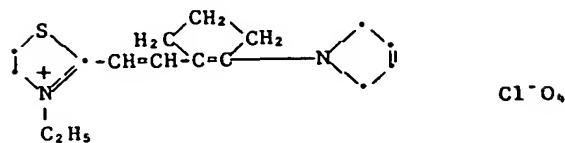
Some representative blue sensitizing hemicyanine dyes are listed below in Table III.

Table III

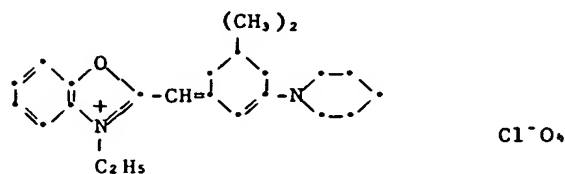
- 1 5,6-Dichloro-2-[4-(diethylamino)-1,3-butadien-1-yl]-1,3-diethylbenzimidazolium iodide



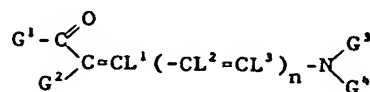
- 2 2-[2-[2-(3-Pyrrolino)-1-cyclopenten-1-yl]ethenyl]-3-ethylthiazolinium perchlorate



- 3 2-(5,5-Dimethyl-3-piperidino-2-cyclohexen-1-ylidenemethyl)-3-ethylbenzoxazolium perchlorate



Useful blue sensitizing hemioxonol dyes include those represented by Formula 4.



Formula 4

where

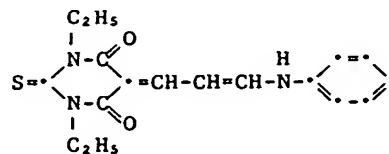
G¹ and G² represent the same elements as in Formula 2; G³, G⁴, L¹, L², and L³ represent the same elements as in Formula 3; and

n is 0 or 1.

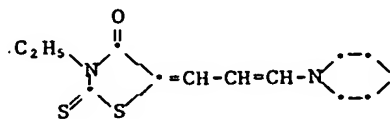
Some representative blue sensitizing hemioxonol dyes are listed in Table IV.

Table IV

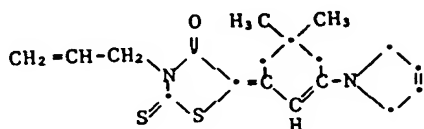
- 1 5-(3-Anilino-2-propen-1-ylidene)-1,3-diethyl-2-thiobarbituric acid



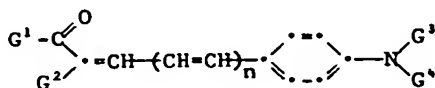
- 2 3-Ethyl-5-(3-piperidino-2-propen-1-ylidene)rhodanine



- 3 3-Allyl-5-[5,5-dimethyl-3-(3-pyrrolino)-2-cyclohexen-1-ylidene]rhodanine



Useful blue sensitizing merostyryl dyes include those represented by Formula 5.



Formula 5

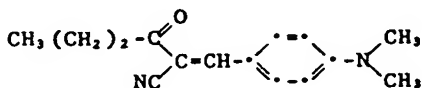
where

G^1 , G^2 , G^3 , G^4 , and n are as defined in Formula 4.

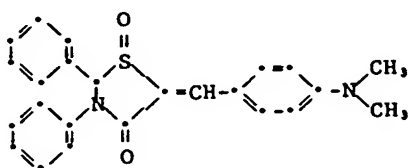
Some representative blue sensitizing merostyryl dyes are listed in Table V.

Table V

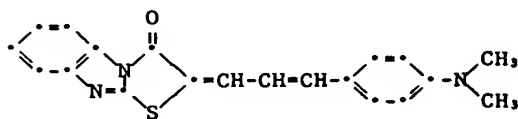
- 1 1-Cyano-1-(4-dimethylaminobenzylidene)-2-pentanone



- 2 5-(4-Dimethylaminobenzylidene)-2,3-diphenylthiazolidin-4-one-1-oxide



- 3 2-(4-Dimethylaminocinnamylidene)thiazolo-[3,2-a]-benzimidazol-3-one



Spectral sensitization can be undertaken at any stage of emulsion preparation heretofore known to be useful. Most commonly spectral sensitization is undertaken in the art subsequent to the completion of chemical sensitization. However, it is specifically recognized that spectral sensitization can be undertaken alternatively concurrently with chemical sensitization, can entirely precede chemical sensitization, and can even commence prior to the completion of silver halide grain precipitation, as taught by Philippaerts et al US Patent 3,628,960, and Locker et al US Patent 4,225,666. As taught by Locker et al, it is specifically contemplated to distribute introduction of the spectral sensitizing dye into the emulsion so that a portion of the spectral sensitizing dye is present prior to chemical sensitization and a remaining portion is introduced after chemical sensitization. Unlike Locker et al, it is specifically contemplated that the spectral sensitizing dye can be added to the emulsion after 80 percent of the silver halide has been precipitated. Sensitization can be enhanced by pAg adjustment, including variation in pAg which completes one or more cycles, during chemical and/or spectral sensitization. A specific example of pAg adjustment is provided by *Research Disclosure*, Vol 181, May 1979, Item 18155.

Chemical sensitization effects can be achieved by epitaxial deposition onto high aspect ratio tabular grain emulsion host grains. Soluble silver salts, such as silver acetate, silver trifluoroacetate, and silver nitrate can be introduced capable of reacting with a soluble halide salt to effect epitaxial deposition. Alternatively silver salts capable of directly precipitating onto high aspect ratio tabular grain emulsion grain surfaces, such as silver thiocyanate, silver phosphate, silver carbonate, and the like, can be introduced. Fine silver halide (ie, silver bromide, iodide, and/or chloride) grains capable of Ostwald ripening onto the tabular grain surfaces can be introduced. For example, a Lippmann emulsion can be introduced to effect epitaxial deposition. Epitaxial deposition at selected edge and corner sites is preferred. It is specifically contemplated to undertake epitaxial deposition onto the tabular host grains in the presence of a site director. Iodide ions can act as a site director for epitaxial deposition. Epitaxial deposition onto the host grains following spectral sensitization is specifically contemplated.

It has been discovered that high aspect ratio tabular grain silver halide emulsions can exhibit better speed-granularity relationships when chemically and spectrally sensitized than have heretofore been achieved using conventional silver halide emulsions of like halide content. It is generally known in the art that silver bromide emulsions produce the best achievable speed-granularity relationships. Therefore, such emulsions are used to satisfy commercial camera-speed photographic applications. Substantially optimally chemically and spectrally sensitized high aspect ratio tabular grain silver bromide emulsions exhibit improved speed-granularity relationships as compared to the best speed-granularity relationships heretofore achieved in the art. More generally, substantially optimally chemically and spectrally sensitized high aspect ratio tabular grain emulsions when exposed within a region of spectral sensitization exhibit improvements in speed-granularity relationships as compared to conventional emulsions of similar halide content. Improved speed-granularity relationships are specifically contemplated for high aspect ratio tabular grain silver bromide and silver bromide emulsions spectrally sensitized and exposed in the green and / or red portions of the spectrum. Improvements in the speed-granularity relationships in the native sensitivity region of the spectrum (eg, the blue portion of the spectrum) can also be realized using blue spectral sensitizing dyes when the high aspect ratio tabular grains of this disclosure are compared to similarly sensitized conventional (ie, low aspect ratio tabular or non-tabular) silver halide grains of comparable individual grain volume.

Although not required to realize all of their advantages, the emulsions of the present disclosure are preferably, in accordance with prevailing manufacturing practices, substantially optimally chemically and spectrally sensitized. That is, they preferably achieve speeds of at least 60 percent of the maximum log speed obtainable from the grains in the spectral region of sensitization under the contemplated conditions of use and processing. Log speed is herein defined as $100(1 - \log E)$, where E is measured in meter-candle-seconds at a density of 0.1 above fog. Once the silver halide grains of an emulsion layer have been characterized, it is possible to estimate from further product analysis and performance evaluation whether an emulsion layer of a product appears to be substantially optimally chemically and spectrally sensitized in relation to comparable commercial offerings of other manufacturers. To achieve the sharpness advantages of the present disclosure it is immaterial whether the silver halide emulsions are chemically or spectrally sensitized.

Once high aspect ratio tabular grain emulsions have been generated by precipitation procedures, washed, and sensitized, as described above, their preparation can be completed by the incorporation of conventional photographic addenda, and they can be usefully applied to photographic applications requiring a silver image to be produced — eg, conventional black-and-white photography.

Hardening photographic elements according to the present disclosure intended to form silver images to an extent sufficient to obviate the necessity of incorporating additional hardener during processing permits increased silver covering power to be realized as compared to photographic elements similarly hardened and processed, but employing nontabular or less than high aspect ratio tabular grain emulsions. Specifically, it is taught to harden the high aspect ratio tabular grain emulsion layers and other hydrophilic colloid layers of black-and-white photographic elements in an amount sufficient to reduce swelling of the layers to less than 200 percent, percent swelling being determined by (a) incubating the photographic element at 38°C for 3 days at 50 percent relative humidity, (b) measuring layer thickness, (c) immersing the photographic element in distilled water at 21°C for 3 minutes, and (d) measuring change in layer thickness. Although hardening of the photographic elements intended to form silver images to the extent that hardeners need not be incorporated in processing solutions is specifically preferred, it is recognized that the emulsions of the present disclosure can be hardened to any conventional level. It is further specifically contemplated to incorporate hardeners in processing solutions, as illustrated, for example, by *Research Disclosure*, Vol

184, August 1979, Item 18431, Paragraph K, relating particularly to the processing of radiographic materials.

Typical useful incorporated hardeners (forehardeners) include formaldehyde and free dialdehydes, such as succinaldehyde and glutaraldehyde, as illustrated by Allen et al US Patent 3,232,764; blocked dialdehydes, as illustrated by Kaszuba US Patent 2,586,168, Jeffreys US Patent 2,870,013, and Yamamoto et al US Patent 3,819,608; α -diketones, as illustrated by Allen et al US Patent 2,725,305; active esters of the type described by Burness et al US Patent 3,542,558; sulfonate esters, as illustrated by Allen et al US Patents 2,725,305 and 2,726,162; active halogen compounds, as illustrated by Burness US Patent 3,106,468, Silverman et al US Patent 3,839,042, Ballantine et al US Patent 3,951,940 and Himmelmann et al US Patent 3,174,861; s-triazines and diazines, as illustrated by Yamamoto et al US Patent 3,325,287, Anderau et al US Patent 3,288,775 and Stauner et al US Patent 3,992,366; epoxides, as illustrated by Allen et al US Patent 3,047,394, Burness US Patent 3,189,459 and Birr et al German Patent 1,085,663; aziridines, as illustrated by Allen et al US Patent 2,950,197, Burness et al US Patent 3,271,175 and Sato et al US Patent 3,575,705; active olefins having two or more active vinyl groups (eg vinylsulfonyl groups), as illustrated by Burness et al US Patents 3,490,911, 3,539,644 and 3,841,872 (Reissue 29,305), Cohen US Patent 3,640,720, Kleist et al German Patent 872,153 and Allen US Patent 2,992,109; blocked active olefins, as illustrated by Burness et al US Patent 3,360,372 and Wilson US Patent 3,345,177; carbodiimides, as illustrated by Blout et al German Patent 1,148,446; isoxazolium salts unsubstituted in the 3-position, as illustrated by Burness et al US Patent 3,321,313; esters of 2-alkoxy-N-carboxyhydroquinoline, as illustrated by Berghaller et al US Patent 4,013,468; N-carbamoyl and N-carbamoyloxypyridinium salts, as illustrated by Himmelmann US Patent 3,880,665; hardeners of mixed function, such as halogen-substituted aldehyde acids (eg, mucochloric and mucobromic acids), as illustrated by White US Patent 2,080,019, 'onium substituted acroleins, as illustrated by Tschopp et al US Patent 3,792,021, and vinyl sulfones containing other hardening functional groups, as illustrated by Sera et al US Patent 4,028,320; and polymeric hardeners, such as dialdehyde starches, as illustrated by Jeffreys et al US Patent 3,057,723, and copoly(acrolein-methacrylic acid), as illustrated by Himmelmann et al US Patent 3,396,029.

The use of forehardeners in combination is illustrated by Sieg et al US Patent 3,497,358, Dallan et al US Patent 3,832,181 and 3,840,370 and Yamamoto et al US Patent 3,898,089. Hardening accelerators can be used, as illustrated by Sheppard et al US Patent 2,165,421, Kleist German Patent 881,444, Riebel et al US Patent 3,628,961 and Ugi et al US Patent 3,901,708. The patents illustrative of hardeners and hardener combinations are here incorporated by reference.

Instability which increases minimum density in negative type emulsion coatings (ie, fog) or which increases minimum density or decreases maximum density in direct-positive emulsion coatings can be protected against by incorporation of stabilizers, antifogants, antikinking agents, latent image stabilizers and similar addenda in the emulsion and contiguous layers prior to coating. Many of the antifogants which are effective in emulsions can also be used in developers and can be classified under a few general headings, as illustrated by C E K Mees, *The Theory of the Photographic Process*, 2nd Ed, Macmillan, 1954, pp 677-680.

To avoid such instability in emulsion coatings stabilizers and antifogants can be employed, such as halide ions (eg, bromide salts); chloropalladates and chloropalladites, as illustrated by Trivelli et al US Patent 2,566,263; water-soluble inorganic salts of magnesium, calcium, cadmium, cobalt, manganese and zinc, as illustrated by Jones US Patent 2,839,405 and Sidebotham US Patent 3,488,709; mercury salts, as illustrated by Allen et al US Patent 2,728,663; selenols and diselenides, as illustrated by Brown et al UK Patent 1,336,570 and Pollet et al UK Patent 1,282,303; quaternary ammonium salts of the type illustrated by Allen et al US Patent 2,694,716, Brooker et al US Patent 2,131,038, Graham US Patent 3,342,596 and Arai et al US Patent 3,954,478; azomethine desensitizing dyes, as illustrated by Thiers et al US Patent 3,630,744; isothiourea derivatives, as illustrated by Herz et al US Patent 3,220,839 and Knott et al US Patent 2,514,650; thiazolidines, as illustrated by Scavron US Patent 3,565,625; peptide derivatives, as illustrated by Maffet US Patent 3,274,002; pyrimidines and 3-pyrazolidones, as illustrated by Welsh US Patent 3,161,515 and Hood et al US Patent 2,751,297; azotriazoles and azotetrazoles, as illustrated by Baldassarri et al US Patent 3,925,086; azaindenes, particularly tetraazaindenes, as illustrated by Heimbach US Patent 2,444,605, Knott US Patent 2,933,388, Williams US Patent 3,202,512, *Research Disclosure*, Vol 134, June 1975, Item 13452, and Vol 148, August 1976, Item 14851, and Nepker et al UK Patent 1,338,567; mercaptotetrazoles, -triazoles and -diazoles, as illustrated by Kendall et al US Patent 2,403,927, Kennard et al US Patent 3,266,897, *Research Disclosure*, Vol 116, December 1973, Item 11684, Luckey et al US Patent 3,397,987 and Salesin US Patent 3,708,303; azoles, as illustrated by Peterson et al US Patent 2,271,229 and *Research Disclosure*, Item 11684, cited above;

purines, as illustrated by Sheppard et al US Patent 2,319,090, Birr et al US Patent 2,152,460, *Research Disclosure*, Item 13452, cited above, and Dostes et al French Patent 2,296,204 and polymers of 1,3-dihydroxy- (and/or 1,3-carbamoxy)-2-methylenepropene, as illustrated by Saleck et al US Patent 3,926,635.

Among useful stabilizers for gold sensitized emulsions are water-insoluble gold compounds of benzothiazole, benzoxazole, naphthothiazole and certain merocyanine and cyanine dyes, as illustrated by Ytuzio et al US Patent 2,597,915, and sulfonamides, as illustrated by Nishio et al US Patent 3,498,792.

Among useful stabilizers in layers containing poly(alkylene oxides) are tetraazaindenes, particularly in combination with Group VIII noble metals or resorcinol derivatives, as illustrated by Carroll et al US Patent 2,716,062, UK Patent 1,466,024 and Habu et al US Patent 3,929,486; quaternary ammonium salts of the type illustrated by Piper US Patent 2,886,437; water-insoluble hydroxides, as illustrated by Maffet US Patent 2,953,455; phenols, as illustrated by Smith US Patents 2,955,037 and '038; ethylene diurea, as illustrated by Dersch US Patent 3,582,346; barbituric acid derivatives, as illustrated by Wood US Patent 3,617,290; boranes, as illustrated by Bigelow US Patent 3,725,078; 3-pyrazolidinones, as illustrated by Wood UK Patent 1,158,059 and aldioximes, amides, anilides and esters, as illustrated by Butler et al UK Patent 988,052.

The emulsions can be protected from fog and desensitization caused by trace amounts of metals such as copper, lead, tin, iron and the like, by incorporating addenda, such as sulfocatechol-type compounds, as illustrated by Kennard et al US Patent 3,236,652; aldioximes, as illustrated by Carroll et al UK Patent 623,448 and *meta*- and poly phosphates, as illustrated by Draibach US Patent 2,239,284, and carboxylic acids such as ethylenediamine tetraacetic acid, as illustrated by UK Patent 691,715.

Among stabilizers useful in layers containing synthetic polymers of the type employed as vehicles and to improve covering power are monohydric and polyhydric phenols, as illustrated by Forsgard US Patent 3,043,697; saccharides, as illustrated by UK Patent 897,497 and Stevens et al UK Patent 1,039,471 and quinoline derivatives, as illustrated by Dersch et al US Patent 3,446,618.

Among stabilizers useful in protecting the emulsion layers against dichroic fog are addenda, such as salts of nitron, as illustrated by Barbier et al US Patents 3,679,424 and 3,820,998; mercaptocarboxylic acids, as illustrated by Willems et al US Patent 3,600,178, and addenda listed by E J Birr *Stabilization of Photographic Silver Halide Emulsions*, Focal Press, London 1974, pp 126-218.

Among stabilizers useful in protecting emulsion layers against development fog are addenda such as azabenzimidazoles, as illustrated by Bloom et al UK Patent 1,356,142 and US Patent 3,575,699, Rogers US Patent 3,473,924 and Carlson et al US Patent 3,649,267; substituted benzimidazoles, benzothiazoles, benzotriazoles and the like, as illustrated by Brooker et al US Patent 2,131,038, Land US Patent 2,704,721, Rogers et al US Patent 3,265,498; mercaptosubstituted compounds, eg, mercaptotetrazoles, as illustrated by Dimsdale et al US Patent 2,432,864, Rauch et al US Patent 3,081,170, Weyerts et al US Patent 3,260,597, Grasshoff et al US Patent 3,674,478 and Arond US Patent 3,706,557; isothiourea derivatives, as illustrated by Herz et al US Patent 3,220,839, and thiodiazole derivatives, as illustrated by von Konig US Patent 3,364,028 and von Konig et al UK Patent 1,186,441.

Where hardeners of the aldehyde type are employed, the emulsion layers can be protected with antifogants, such as monohydric and polyhydric phenols of the type illustrated by Sheppard et al US Patent 2,165,421; nitro-substituted compounds of the type disclosed by Rees et al UK Patent 1,269,268; poly(alkylene oxides), as illustrated by Valbusa UK Patent 1,151,914, and mucohalogenic acids in combination with urazoles, as illustrated by Allen et al US Patents 3,232,761 and 3,232,764, or further in combination with maleic acid hydrazide, as illustrated by Rees et al US Patent 3,295,980.

To protect emulsion layers coated on linear polyester supports addenda can be employed such as parabanic acid, hydantoin acid hydrazides and urazoles, as illustrated by Anderson et al US Patent 3,287,135, and piazines containing two symmetrically fused 6-member carbocyclic rings, especially in combination with an aldehyde-type hardening agent, as illustrated in Rees et al US Patent 3,396,023.

Kink desensitization of the emulsions can be reduced by the incorporation of thallos nitrate, as illustrated by Overman US Patent 2,628,167; compounds, polymeric latices and dispersions of the type disclosed by Jones et al US Patents 2,759,821 and '822; azole and mercaptotetrazole hydrophilic colloid dispersions of the type disclosed by *Research Disclosure*, Vol 116, December 1973, Item 11684; plasticized gelatin compositions of the type disclosed by Milton et al US Patent 3,033,680; water-soluble interpolymers of the type disclosed by Rees et al US Patent 3,536,491; polymeric latices prepared by emulsion polymerization in the presence of poly(alkylene oxide), as disclosed by Pearson et al US Patent 3,772,032, and gelatin graft copolymers of the type disclosed by Rakoczy US

Patent 3,837,861.

Where the photographic element is to be processed at elevated bath or drying temperatures, as in rapid access processors, pressure desensitization and/or increased fog can be controlled by selected combinations of addenda, vehicles, hardeners and/or processing conditions, as illustrated by Abbott et al US Patent 3,295,976, Barnes et al US Patent 3,545,971, Salesin US Patent 3,708,303, Yamamoto et al US Patent 3,615,619, Brown et al US Patent 3,623,873, Taber US Patent 3,671,258, Abele US Patent 3,791,830, *Research Disclosure*, Vol 99, July 1972, Item 9930, Florens et al US Patent 3,843,364, Priem et al US Patent 3,867,152, Adachi et al US Patent 3,967,965 and Mikawa et al US Patents 3,947,274 and 3,954,474.

In addition to increasing the pH or decreasing the pAg of an emulsion and adding gelatin, which are known to retard latent image fading, latent image stabilizers can be incorporated, such as amino acids, as illustrated by Ezekiel UK Patents 1,335,923, 1,378,354, 1,387,654 and 1,391,672, Ezekiel et al UK Patent 1,394,371, Jefferson US Patent 3,843,372, Jefferson et al UK Patent 1,412,294 and Thurston UK Patent 1,343,904; carbonyl-bisulfite addition products in combination with hydroxybenzene or aromatic amine developing agents, as illustrated by Seiter et al US Patent 3,424,583; cycloalkyl-1,3-diones, as illustrated by Beckett et al US Patent 3,447,926; enzymes of the catalase type, as illustrated by Matejec et al US Patent 3,600,182; halogen-substituted hardeners in combination with certain cyanine dyes, as illustrated by Kumai et al US Patent 3,881,933; hydrazides, as illustrated by Honig et al US Patent 3,386,831; alkenylbenzothiazolium salts, as illustrated by Arai et al US Patent 3,954,478; soluble and sparingly soluble mercaptides, as illustrated by Herz US Serial No 236,360, filed February 20, 1981, commonly assigned and here incorporated by reference; hydroxy-substituted benzylidene derivatives, as illustrated by Thurston UK Patent 1,398,777 and Ezekiel et al UK Patents 1,347,544 and 1,353,527; mercapto-substituted compounds of the type disclosed by Sutherns US Patent 3,519,427; metal-organic complexes of the type disclosed by Matejec et al US Patent 3,639,128; penicillin derivatives, as illustrated by Ezekiel UK Patent 1,389,089; propynylthio derivatives of benzimidazoles, pyrimidines, etc, as illustrated by von Konig et al US Patent 3,910,791; combinations of iridium and rhodium compounds, as disclosed by Yamasue et al US Patent 3,901,713; sydnone or sydnone imines, as illustrated by Noda et al US Patent 3,881,939; thiazolidine derivatives, as illustrated by Ezekiel UK Patent 1,458,197 and thioether-substituted imidazoles, as illustrated by *Research Disclosure*, Vol 136, August 1975, Item 13651.

In addition to sensitizers, hardeners, and antifoggants and stabilizers, a variety of other conventional photographic addenda can be present. The specific choice of addenda depends upon the exact nature of the photographic application and is well within the capability of the art. A variety of useful addenda are disclosed in *Research Disclosure*, Vol 176, December 1978, Item 17643, here incorporated by reference. Optical brighteners can be introduced, as disclosed by Item 17643 at Paragraph V. Absorbing and scattering materials can be employed in the emulsions of the disclosure and in separate layers of the photographic elements, as described in Paragraph VIII. Coating aids, as described in Paragraph XI, and plasticizers and lubricants, as described in Paragraph XII, can be present. Antistatic layers, as described in Paragraph XIII, can be present. Methods of addition of addenda are described in Paragraph XIV. Matting agents can be incorporated, as described in Paragraph XVI. Developing agents and development modifiers can, if desired, be incorporated, as described in Paragraphs XX and XXI. When the photographic elements of the disclosure are intended to serve radiographic applications, emulsion and other layers of the radiographic element can take any of the forms specifically described in *Research Disclosure*, Item 18431, cited above, here incorporated by reference. The emulsions of the disclosure, as well as others, conventional silver halide emulsion layers, interlayers, overcoats, and subbing layers, if any, present in the photographic elements can be coated and dried as described in Item 17643, Paragraph XV.

In accordance with established practices within the art it is specifically contemplated to blend the high aspect ratio tabular grain emulsions of the present disclosure with each other or with conventional emulsions to satisfy specific emulsion layer requirements. For example, it is known to blend emulsions to adjust the characteristic curve of a photographic element to satisfy a predetermined aim. Blending can be employed to increase or decrease maximum densities realized on exposure and processing, to decrease or increase minimum density, and to adjust characteristic curve shape intermediate its toe and shoulder. To accomplish this the emulsions of this disclosure can be blended with conventional silver halide emulsions, such as those described in Item 17643, cited above, Paragraph I. It is specifically contemplated to blend the emulsions as described in sub-paragraph F of Paragraph I. When a relatively fine grain silver chloride emulsion is blended with or coated adjacent the emulsions of the present disclosure, particularly the silver bromoiodide emulsions, a further increase in the contrast and/or sensitivity — ie, speed granularity relationship — of the emulsion can result, as taught by Russell US Patent 3,140,179

and Godowsky US Patent 3,152,907.

In their simplest form photographic elements according to the present disclosure employ a single silver halide emulsion layer containing a high aspect ratio tabular grain emulsion according to the present disclosure and a photographic support. It is, of course, recognized that more than one silver halide emulsion layer as well as overcoat, subbing, and interlayers can be usefully included. Instead of blending emulsions as described above the same effect can usually be achieved by coating the emulsions to be blended as separate layers. Coating of separate emulsion layers to achieve exposure latitude is well known in the art, as illustrated by Zelikman and Levi, *Making and Coating Photographic Emulsions*, Focal Press, 1964, pp 234-238; Wycoff US Patent 3,662,228; and UK Patent 923,045. It is further well known in the art that increased photographic speed can be realized when faster and slower silver halide emulsions are coated in separate layers as opposed to blending. Typically the faster emulsion layer is coated to lie nearer the exposing radiation source than the slower emulsion layer. This approach can be extended to three or more superimposed emulsion layers. Such layer arrangements are specifically contemplated in the practice of this disclosure.

The layers of the photographic elements can be coated on a variety of supports. Typical photographic supports include polymeric film, wood fiber — eg, paper, metallic sheet and foil, glass and ceramic supporting elements provided with one or more subbing layers to enhance the adhesive, antistatic, dimensional, abrasive, hardness, frictional, antihalation and/or other properties of the support surface.

Typical of useful polymeric film supports are films of cellulose nitrate and cellulose esters such as cellulose triacetate and diacetate, polystyrene, polyamides, homo- and co-polymers of vinyl chloride, poly(vinyl acetal), polycarbonate, homo- and co-polymers of olefins, such as polyethylene and polypropylene, and polyesters of dibasic aromatic carboxylic acids with divalent alcohols, such as poly(ethylene terephthalate).

Typical of useful paper supports are those which are partially acetylated or coated with baryta and/or a polyolefin, particularly a polymer of an α -olefin containing 2 to 10 carbon atoms, such as polyethylene, polypropylene, copolymers of ethylene and propylene and the like.

Polyolefins, such as polyethylene, polypropylene and polyallomers — eg, copolymers of ethylene with propylene, as illustrated by Hagemeyer et al US Patent 3,478,128, are preferably employed as resin coatings over paper, as illustrated by Crawford et al US Patent 3,411,908 and Joseph et al US Patent 3,630,740, over polystyrene and polyester film supports, as illustrated by Crawford et al US Patent 3,630,742, or can be employed as unitary flexible reflection supports, as illustrated by Venor et al US Patent 3,973,963.

Preferred cellulose ester supports are cellulose triacetate supports, as illustrated by Fordyce et al US Patents 2,492,977, '978 and 2,739,069, as well as mixed cellulose ester supports, such as cellulose acetate propionate and cellulose acetate butyrate, as illustrated by Fordyce et al US Patent 2,739,070.

Preferred polyester film supports are comprised of linear polyester, such as illustrated by Alles et al US Patent 2,627,088, Wellman US Patent 2,720,503, Alles US Patent 2,779,684 and Kibler et al US Patent 2,901,466. Polyester films can be formed by varied techniques, as illustrated by Alles, cited above, Czerkas et al US Patent 3,663,683 and Williams et al US Patent 3,504,075, and modified for use as photographic film supports, as illustrated by Van Stappen US Patent 3,227,576, Nadeau et al US Patent 3,501,301, Reedy et al US Patent 3,589,905, Babbitt et al US Patent 3,850,640, Bailey et al US Patent 3,888,678, Hunter US Patent 3,904,420 and Mallinson et al US Patent 3,928,697.

The photographic elements can employ supports which are resistant to dimensional change at elevated temperatures. Such supports can be comprised of linear condensation polymers which have glass transition temperatures above about 190°C, preferably 220°C, such as polycarbonates, polycarboxylic esters, polyamides, polysulfonamides, polyethers, polyimides, polysulfonates and copolymer variants, as illustrated by Hamb US Patents 3,634,089 and 3,772,405; Hamb et al US Patents 3,725,070 and 3,793,249; Wilson *Research Disclosure*, Vol 118, February 1974, Item 11833, and Vol 120, April 1974, Item 12046; Conklin et al *Research Disclosure*, Vol 120, April 1974, Item 12012; *Product Licensing Index*, Vol 92, December 1971, Items 9205 and 9207; *Research Disclosure*, Vol 101, September 1972, Items 10119 and 10148; *Research Disclosure*, Vol 106, February 1973, Item 10613; *Research Disclosure*, Vol 117, January 1974, Item 11709, and *Research Disclosure*, Vol 134, June 1975, Item 13455.

Although the emulsion layer or layers are typically coated as continuous layers on supports having opposed planar major surfaces, this need not be the case. The emulsion layers can be coated as laterally displaced layer segments on a planar support surface. When the emulsion layer or layers are segmented, it is preferred to employ a microcellular support. Useful microcellular supports are disclosed by Whitmore Patent Cooperation Treaty published application W080/01614, published August 7, 1980, (Belgian Patent 881,513, August 1, 1980, corresponding), and Blazey et al US

Patent 4,307,165, here incorporated by reference. Microcells can range from 1 to 200 microns in width and up to 1000 microns in depth. It is generally preferred that the microcells be at least 4 microns in width and less than 200 microns in depth, with optimum dimensions being about 10 to 100 microns in width and depth for ordinary black-and-white imaging applications — particularly where the photographic image is intended to be enlarged.

The photographic elements of the present disclosure can be imagewise exposed in any conventional manner. Attention is directed to *Research Disclosure* Item 17643, cited above, Paragraph XVIII, here incorporated by reference. The present disclosure is particularly advantageous when imagewise exposure is undertaken with electromagnetic radiation within the region of the spectrum in which the spectral sensitizers present exhibit absorption maxima. When the photographic elements are intended to record blue, green, red, or infrared exposures, spectral sensitizer absorbing in blue, green, red, or infrared portion of the spectrum is present. For black-and-white imaging applications it is preferred that the photographic elements be orthochromatically or panchromatically sensitized to permit light to extend sensitivity within the visible spectrum. Radiant energy employed for exposure can be either noncoherent (random phase) or coherent (in phase), produced by lasers. Image-wise exposures at ambient, elevated or reduced temperatures and/or pressures, including high or low intensity exposures, continuous or intermittent exposures, exposure times ranging from minutes to relatively short durations in the millisecond to microsecond range and solarizing exposures, can be employed within the useful response ranges determined by conventional sensitometric techniques, as illustrated by T H James, *The Theory of the Photographic Process*, 4th Ed., Macmillan, 1977, Chapters 4, 6, 17, 18, and 23.

The light-sensitive silver halide contained in the photographic elements can be processed following exposure to form a visible image by associating the silver halide with an aqueous alkaline medium in the presence of a developing agent contained in the medium or the element. Processing formulations and techniques are described in L F Mason, *Photographic Processing Chemistry*, Focal Press, London, 1966; *Processing Chemicals and Formulas*, Publication J-1, Eastman Kodak Company, 1973; *Photo-Lab Index*, Morgan and Morgan, Inc., Dobbs Ferry, New York, 1977, and *Neblette's Handbook of Photography and Reprography — Materials, Processes and Systems*, VanNostrand Reinhold Company, 7th Ed., 1977.

Included among the processing methods are web processing, as illustrated by Tregillus et al US Patent 3,179,517; stabilization processing, as illustrated by Herz et al US Patent 3,220,839, Cole US Patent 3,615,511, Shipton et al UK Patent 1,258,906 and Haist et al US Patent 3,647,453; monobath processing as described in Haist, *Monobath Manual*, Morgan and Morgan, Inc., 1966, Schuler US Patent 3,240,603, Haist et al US Patents 3,615,513 and 3,628,955 and Price US Patent 3,723,126; infectious development, as illustrated by Milton US Patents 3,294,537, 3,600,174, 3,615,519 and 3,615,524, Whiteley US Patent 3,516,830, Drago US Patent 3,615,488, Salesin et al US Patent 3,625,689, Illingsworth US Patent 3,632,340, Salesin UK Patent 1,273,030 and US Patent 3,708,303; hardening development, as illustrated by Allen et al US Patent 3,232,761; roller transport processing, as illustrated by Russell et al US Patents 3,025,779 and 3,515,556, Masseth US Patent 3,573,914, Taber et al US Patent 3,647,459 and Rees et al UK Patent 1,269,268; alkaline vapor processing, as illustrated by *Product Licensing Index*, Vol 97, May 1972, Item 9711, Goffe et al US Patent 3,816,136 and King US Patent 3,985,564; metal ion development as illustrated by Price, *Photographic Science and Engineering*, Vol 19, Number 5, 1975, pp 283-287 and Vought *Research Disclosure*, Vol 150, October 1976, Item 15034; reversal processing, as illustrated by Henn et al US Patent 3,576,633; and surface application processing, as illustrated by Kitze US Patent 3,418,132.

Once a silver image has been formed in the photographic element, it is conventional practice to fix the undeveloped silver halide. The high aspect ratio tabular grain emulsions of the present disclosure are particularly advantageous in allowing fixing to be accomplished in a shorter time period. This allows processing to be accelerated.

The photographic elements and the techniques described above for producing silver images can be readily adapted to provide a coloured image through the use of dyes. In perhaps the simplest approach to obtaining a projectable color image a conventional dye can be incorporated in the support of the photographic element, and silver image formation undertaken as described above. In areas where a silver image is formed the element is rendered substantially incapable of transmitting light therethrough, and in the remaining areas light is transmitted corresponding in color to the color of the support. In this way a colored image can be readily formed. The same effect can also be achieved by using a separate dye filter layer or element with a transparent support element.

The silver halide photographic elements can be used to form dye images therein through the selective destruction or formation of dyes. The photographic elements described above for forming silver images can be used to form dye images by employing develop-

ers containing dye image formers, such as color couplers, as illustrated by UK Patent 478,984, Yager et al US Patent 3,113,864, Vittum et al US Patents 3,002,836, 2,271,238 and 2,362,598, Schwan et al US Patent 2,950,970, Carroll et al US Patent 2,592,243, Porter et al US Patents 2,343,703, 2,376,380 and 2,369,489, Spath UK Patent 886,723 and US Patent 2,899,306, Tuite US Patent 3,152,896 and Mannes et al US Patents 2,115,394, 2,252,718 and 2,108,602, and Pilato US Patent 3,547,650. In this form the developer contains a color-developing agent (eg, a primary aromatic amine) which in its oxidized form is capable of reacting with the coupler (coupling) to form the image dye.

The dye-forming couplers can be incorporated in the photographic elements, as illustrated by Schneider et al, *Die Chemie*, Vol 57, 1944, p 113, Mannes et al US Patent 2,304,940, Martinez US Patent 2,269,158, Jelley et al US Patent 2,322,027, Frolich et al US Patent 2,376,679, Fierke et al US Patent 2,801,171, Smith US Patent 3,748,141, Tong US Patent 2,772,163, Thirtle et al US Patent 2,835,579, Sawdey et al US Patent 2,533,514, Peterson US Patent 2,353,754, Seidel US Patent 3,409,435 and Chen *Research Disclosure*, Vol 159, July 1977, Item 15930. The dye-forming couplers can be incorporated in different amounts to achieve differing photographic effects. For example, UK Patent 923,045 and Kumai et al US Patent 3,843,369 teach limiting the concentration of coupler in relation to the silver coverage to less than normally employed amounts in faster and intermediate speed emulsion layers.

The dye-forming couplers are commonly chosen to form subtractive primary (ie, yellow, magenta and cyan) image dyes and are nondiffusible, colorless couplers, such as two and four equivalent couplers of the open chain ketomethylene, pyrazolone, pyrazolotriazole, pyrazolobenzimidazole, phenol and naphthol type hydrophobically ballasted for incorporation in high-boiling organic (coupler) solvents. Such couplers are illustrated by Salminen et al US Patents 2,423,730, 2,772,162, 2,895,826, 2,710,803, 2,407,207, 3,737,316 and 2,367,531, Loria et al US Patents 2,772,161, 2,600,788, 3,006,759, 3,214,437 and 3,253,924, McCrossen et al US Patent 2,875,057, Bush et al US Patent 2,908,573, Gledhill et al US Patent 3,034,892, Weissberger et al US Patents 2,474,293, 2,407,210, 3,062,653, 3,265,506 and 3,384,657, Porter et al US Patent 2,343,703, Greenhalgh et al US Patent 3,127,269, Feniak et al US Patents 2,865,748, 2,933,391 and 2,865,751, Bailey et al US Patent 3,725,067, Beavers et al US Patent 3,758,308, Lau US Patent 3,779,763, Fernandez US Patent 3,785,829, UK Patent 969,921, UK Patent 1,241,069, UK Patent 1,011,940, Vanden Eynde et al US Patent 3,762,921, Beavers US Patent 2,983,608, Loria US Patents 3,311,476, 3,408,194, 3,458,315, 3,447,928, 3,476,563, Cressman et al US Patent 3,419,390, Young US Patent 3,419,391, Lestina US Patent 3,519,429, UK Patent 975,928, UK Patent 1,111,554, Jaeken US Patent 3,222,176 and Canadian Patent 726,651, Schulte et al UK Patent 1,248,924 and Whitmore et al US Patent 3,227,550. Dye-forming couplers of differing reaction rates in single or separate layers can be employed to achieve desired effects for specific photographic applications.

The dye-forming couplers upon coupling can release photographically useful fragments, such as development inhibitors or accelerators, bleach accelerators, developing agents, silver halide solvents, toners, hardeners, fogging agents, antifoggants, competing couplers, chemical or spectral sensitizers and desensitizers. Development inhibitor-releasing (DIR) couplers are illustrated by Whitmore et al US Patent 3,148,062, Barr et al US Patent 3,227,554, Barr US Patent 3,733,201, Sawdey US Patent 3,617,291, Groet et al US Patent 3,703,375, Abbott et al US Patent 3,615,506, Weissberger et al US Patent 3,265,506, Seymour US Patent 3,620,745, Marx et al US Patent 3,632,345, Mader et al US Patent 3,869,291, UK Patent 1,201,110, Oishi et al US Patent 3,642,485, Verbrugge UK Patent 1,236,767, Fujiwhara et al US Patent 3,770,436 and Matsuo et al US Patent 3,808,945. Dye-forming couplers and non dye-forming compounds which upon coupling release a variety of photographically useful groups are described by Lau US Patent 4,248,962, Kato et al UK 2080963A. Watanabe et al UK 2,038,013A, *Research Disclosure*, Vol 212, Dec 1981, 21228, Venura Japanese 57-56837 and Japanese 56-137353. DIR compounds which do not form dye upon reaction with oxidized color-developing agents can be employed, as illustrated by Fujiwhara et al German OLS 2,529,350 and US Patents 3,928,041, 3,958,993 and 3,961,959, Odenwalder et al German OLS 2,448,063, Tanaka et al German OLS 2,610,546, Kikuchi et al US Patent 4,049,455 and Credner et al US Patent 4,052,213. DIR compounds which oxidatively cleave can be employed, as illustrated by Porter et al US Patent 3,379,529, Green et al US Patent 3,043,690, Barr US Patent 3,364,022, Duennebier et al US Patent 3,297,445 and Rees et al US Patent 3,287,129. Silver halide emulsions which are relatively light insensitive, such as Lippmann emulsions, have been utilized as interlayers and overcoat layers to prevent or control the migration of development inhibitor fragments as described in Shiba et al US Patent 3,892,572.

The photographic elements can incorporate colored dye-forming couplers, such as those employed to form integral masks

for negative color images, as illustrated by Hanson US Patent 2,449,966, Glass et al US Patent 2,521,908, Gledhill et al US Patent 3,034,892, Loria US Patent 3,476,563, Lestina US Patent 3,519,429, Friedman US Patent 2,543,691, Puschel et al US Patent 3,028,238, Menzel et al US Patent 3,061,432 and Greenhalgh UK Patent 1,035,959, and/or competing couplers, as illustrated by Murin et al US Patent 3,876,428, Sakamoto et al US Patent 3,580,722, Puschel US Patent 2,998,314, Whitmore US Patent 2,808,329, Salminen US Patent 2,742,832 and Weller et al US Patent 2,689,793.

The photographic elements can include image dye stabilizers. Such image dye stabilizers are illustrated by UK Patent 1,326,889, Lestina et al US Patents 3,432,300 and 3,698,909, Stern et al US Patent 3,574,627, Brännock et al US Patent 3,573,050, Arai et al US Patent 3,764,337 and Smith et al US Patent 4,042,394.

Dye images can be formed or amplified by processes which employ in combination with a dye image-generating reducing agent an inert transition metal ion complex oxidizing agent, as illustrated by Bissonette US Patents 3,748,138, 3,826,652, 3,862,842 and 3,989,526 and Travis US Patent 3,765,891, and/or a peroxide oxidizing agent, as illustrated by Matejcek US Patent 3,674,490, *Research Disclosure*, Vol 116, December 1973, Item 11660, and Bissonette *Research Disclosure*, Vol 148, August 1976, Items 14836, 14846 and 14847. The photographic elements can be particularly adapted to form dye images by such processes, as illustrated by Dunn et al US Patent 3,822,129, Bissonette US Patents 3,834,907 and 3,902,905, Bissonette et al US Patent 3,847,619 and Mowrey US Patent 3,904,413.

The photographic elements can produce dye images through the selective destruction of dyes or dye precursors, such as silver-dye-bleach processes, as illustrated by A Meyer, *The Journal of Photographic Science*, Vol 13, 1965, pp 90-97. Bleachable azo, azoxy, xanthene, azine, phenylmethane, nitroso complex, indigo, quinone, nitro-substituted, phthalocyanine and formazan dyes, as illustrated by Stauner et al US Patent 3,754,923, Piller et al US Patent 3,749,576, Yoshida et al US Patent 3,738,839, Froelich et al US Patent 3,716,368, Piller US Patent 3,655,388, Williams et al US Patent 3,642,482, Gilman US Patent 3,567,448, Loeffel US Patent 3,443,953, Anderau US Patents 3,443,952 and 3,211,556, Mory et al US Patents 3,202,511 and 3,178,291 and Anderau et al US Patents 3,178,285 and 3,178,290, as well as their hydrazo, diazonium and tetrazolium precursors and leuco and shifted derivatives, as illustrated by UK Patents 923,265, 999,996 and 1,042,300, Pelz et al US Patent 3,684,513, Watanabe et al US Patent 3,615,493, Wilson et al US Patent 3,503,741, Boes et al US Patent 3,340,059, Gompf et al US Patent 3,493,372 and Puschel et al US Patent 3,561,970, can be employed.

It is common practice in forming dye images in silver halide photographic elements to remove the silver which is developed by bleaching. Such removal can be enhanced by incorporation of a bleach accelerator or a precursor thereof in a processing solution or in a layer of the element. In some instances the amount of silver formed by development is small in relation to the amount of dye produced, particularly in dye image amplification, as described above, and silver bleaching is omitted without substantial visual effect. In still other applications the silver image is retained and the dye image is intended to enhance or supplement the density provided by the image silver. In the case of dye enhanced silver imaging it is usually preferred to form a neutral dye or a combination of dyes which together produce a neutral image. Neutral dye-forming couplers useful for this purpose are disclosed by Pupo et al *Research Disclosure*, Vol 162, October 1977, Item 16226. The enhancement of silver images with dyes in photographic elements intended for thermal processing is disclosed in *Research Disclosure*, Vol 173, September 1973, Item 17326, and Houle US Patent 4,137,079. It is also possible to form monochromatic or neutral dye images using only dyes, silver being entirely removed from the image-bearing photographic elements by bleaching and fixing, as illustrated by Marchant et al US Patent 3,620,747.

The photographic elements can be processed to form dye images which correspond to or are reversals of the silver halide rendered selectively developable by imagewise exposure. Reversal dye images can be formed in photographic elements having differentially spectrally sensitized silver halide layers by black-and-white development followed by i) where the elements lack incorporated dye image formers, sequential reversal color development with developers containing dye image formers, such as color couplers, as illustrated by Mannes et al US Patent 2,252,718, Schwen et al US Patent 2,950,970 and Pilato US Patent 3,547,650; ii) where the elements contain incorporated dye image formers, such as color couplers, a single color development step, as illustrated by the Kodak Ektachrome E4 and E6 and Agfa processes described in *British Journal of Photography Annual*, 1977, pp 194-197, and *British Journal of Photography*, August 2, 1974, pp 668-669; and iii) where the photographic elements contain bleachable dyes, silver-dye-bleach processing, as illustrated by the Cibachrome P-10 and P-18 processes described in the *British Journal of Photography Annual*, 1977, pp 209-212.

The photographic elements can be adapted for direct color

reversal processing (ie, production of reversal color images without prior black-and-white development), as illustrated by UK Patent 1,075,385, Barr US Patent 3,243,294, Hendess et al US Patent 3,647,452, Puschel et al German Patent 1,257,570 and US Patents 3,457,077 and 3,467,520, Accary-Venet et al UK Patent 1,132,736, Schranz et al German Patent 1,259,700, Marx et al German Patent 1,259,701 and Muller-Bore German OLS 2,005,091.

Dye images which correspond to the silver halide rendered selectively developable by imagewise exposure, typically negative dye images, can be produced by processing, as illustrated by the Kodacolor C-22, the Kodak Flexicolor C-41 and the Agfacolor processes described in *British Journal of Photography Annual*, 1977, pp 201-205. The photographic elements can also be processed by the Kodak Ektaprint-3 and 300 processes as described in Kodak Color Dataguide, 5th Ed, 1975, pp 18-19, and the Agfa color process as described in *British Journal of Photography Annual*, 1977, pp 205-206, such processes being particularly suited to processing color print materials, such as resin-coated photographic papers, to form positive dye images.

It has been recognized and reported in the art that some photo-detectors exhibit detective quantum efficiencies which are superior to those of silver halide photographic elements. A study of the basic properties of conventional silver halide photographic elements shows that this is largely due to the binary, on-off nature of individual silver halide grains, rather than their low quantum sensitivity. This is discussed, for example, by Shaw, 'Multilevel Grains and the Ideal Photographic Detector', *Photographic Science and Engineering*, Vol 16, No 3, May/June 1972, pp 192-200. What is meant by the on/off nature of silver halide grains is that once a latent image centre is formed on a silver halide grain, the grain becomes entirely developable. Ordinarily development is independent of the amount of light which has struck the grain above a threshold, latent image forming amount. The silver halide grain produces exactly the same product upon development whether it has absorbed many photons and formed several latent image centers or absorbed only the minimum number of photons to produce a single latent image center.

Upon exposure by light, for instance, latent image centers are formed in and on the silver halide grains of the high aspect ratio tabular grain emulsions of this disclosure. Some grains may have only one latent image center, some many and some none. However, the number of latent image centers formed is related to the amount of exposing radiation. Because the tabular grains can be relatively large in diameter and since their speed-granularity relationship can be high, particularly when formed of substantially optimally chemically and spectrally sensitized silver bromide, their speed can be relatively high. Because the number of latent image centers in or on each grain is directly related to the amount of exposure that the grain has received, the potential is present for a high detective quantum efficiency, provided this information is not lost in development.

In a preferred form each latent image center is developed to increase its size without completely developing the silver halide grains. This can be undertaken by interrupting silver halide development at an earlier than usual stage, well before optimum development for ordinary photographic applications has been achieved. Another approach is to employ a DIR coupler and a color developer agent. The inhibitor released upon coupling can be relied upon to prevent complete development of the silver halide grains. In a preferred form of practicing this step self-inhibiting developers are employed. A self-inhibiting developer is one which initiates development of silver halide grains, but itself stops development before the silver grains have been entirely developed. Preferred developers are self-inhibiting developers containing p-phenylenediamines, such as disclosed by Neuberger et al, 'Anomalous Concentration Effect: An Inverse Relationship Between the Rate of Development and Developer Concentration of Some p-Phenylenediamines', *Photographic Science and Engineering*, Vol 19, No 6, Nov-Dec 1975, pp 327-332. Whereas with interrupted development or development in the presence of DIR couplers silver halide grains having a longer development induction period than adjacent developing grains can be entirely precluded from development, the use of a self-inhibiting developer has the advantage that development of an individual silver halide grain is not inhibited until after some development of that grain has occurred.

Development enhancement of the latent image centers produces a plurality of silver specks. These specks are proportional in size and number to the degree of exposure of each grain. Inasmuch as the preferred self-inhibiting developers contain color developing agents, the oxidized developing agent produced can be reacted with a dye-forming coupler to create a dye image. However, since only a limited amount of silver halide is developed, the amount of dye which can be formed in this way is also limited. An approach which removes any such limitation on maximum dye density formation, but which retains the proportionality of dye density to the degree of exposure is to employ a silver catalyzed oxidation-reduction reaction using a peroxide or transition metal ion complex as an oxidizing agent and a dye-image-generating reducing agent, such as a color developing agent, as illustrated by the patents cited above.

of Bissonette, Travis, Dunn et al, Matejec, and Mowrey and the accompanying publications. In these patents it is further disclosed that where the silver halide grains form surface latent image centers the centers can themselves provide sufficient silver to catalyze a dye image amplification reaction. Accordingly, the step of enhancing the latent image by development is not absolutely essential, although it is preferred. In the preferred form any visible silver remaining in the photographic element after forming the dye image is removed by bleaching, as is conventional in color photography.

The resulting photographic image is a dye image which exhibits a point-to-point dye density which is proportional to the amount of exposing radiation. The result is that the detective quantum efficiency of the photographic element is quite high. High photographic speeds are readily obtainable, although oxidation reduction reactions as described above can contribute in increased levels of graininess.

Graininess can be reduced by employing a microcellular support as taught by Whitmore PCT application W080/01614, cited above. The sensation of graininess is created not just by the size of individual image dye clouds, but also by the randomness of their placement. By coating the emulsions in a regular array of microcells formed by the support and smearing the dye produced in each microcell so that it is uniform throughout, a reduced sensation of graininess can be produced.

Although partial grain development has been described above with specific reference to forming dye images, it can be applied to forming silver images as well. In developing to produce a silver image for viewing the graininess of the silver image can be reduced by terminating development before grains containing latent image sites have been completely developed. Since a greater number of silver centers or specks can be produced by partial grain development than by whole grain development, the sensation of graininess at a given density is reduced. (A similar reduction in graininess can also be achieved in dye imaging using incorporated couplers by limiting the concentration of the coupler so that it is present in less than its normally employed stoichiometric relationship to silver halide). Although silver coverages in the photographic element must be initially higher to permit partial grain development to achieve maximum density levels comparable to those of total grain development, the silver halide that is not developed can be removed by fixing and recovered; hence the net consumption of silver need not be increased.

By employing partial grain development in silver imaging of photographic elements having microcellular supports it is possible to reduce silver image graininess similarly as described above in connection with dye imaging. For example, if a silver halide emulsion according to the present disclosure is incorporated in an array of microcells on a support and partially developed after imagewise exposure, a plurality of silver specks are produced proportional to the quanta of radiation received on exposure and the number of latent image sites formed. Although the covering power of the silver specks is low in comparison to that achieved by total grain development, it can be increased by fixing out undeveloped silver halide, rehalogenating the silver present in the microcells, and then physically developing the silver onto a uniform coating of physical development nuclei contained in the microcells. Since silver physically developed onto fine nuclei can have a much higher density than chemically developed silver, a much higher maximum density is readily obtained. Further, the physically developed silver produces a uniform density within each microcell. This produces a reduction in graininess, since the random occurrence of the silver density is replaced by the regularity of the microcell pattern.

When the high aspect ratio tabular grain emulsions of the present disclosure are substantially optimally sensitized as described above within a selected spectral region and the sensitivity of the emulsion within that spectral region is compared to a spectral region to which the emulsion would be expected to possess native sensitivity by reason of its halide composition, it has been observed that a much larger sensitivity difference exists than has heretofore been observed in conventional emulsions. Inadequate separation of blue and green or red sensitivities of silver bromide and silver bromoiodide emulsions has long been a disadvantage in multi-color photography. The advantageous use of the spectral sensitivity differences of the silver bromide and bromoiodide emulsions of this disclosure are illustrated below with specific reference to multi-color photographic elements. It is to be recognized, however, that this is but an illustrative application. The increased spectral sensitivity differences exhibited by the emulsions of the present disclosure are not limited to multi-color photography or to silver bromide or bromoiodide emulsions. It can be appreciated that the spectral sensitivity differences of the emulsions of this disclosure can be observed in single emulsion layer photographic elements. Further, advantages of increased spectral sensitivity differences can be realized with emulsions of any halide composition known to be useful in photography. For example, while silver chloride and chlorobromide emulsions are known to possess sufficiently low native blue sensitivity that they can be used to record green or red light in multi-color photography without

protection from blue light exposure, there are advantages in other applications for increasing the sensitivity difference between different spectral regions. For example, if a high aspect ratio tabular grain silver chloride emulsion is sensitized to infrared radiation and imagewise exposed in the spectral region of sensitization, it can thereafter be processed in light with less increase in minimum density levels because of the reduced sensitivity of the emulsions according to the disclosure in spectral regions free of spectral sensitization. From the foregoing other applications for the high aspect ratio tabular grain emulsions of the present disclosure permitting their large differences in sensitivity as a function of spectral region to be advantageously employed will be readily suggested to those skilled in the art.

The present disclosure can be employed to produce multi-color photographic images. Generally any conventional multi-color imaging element containing at least one silver halide emulsion layer can be improved merely by adding or substituting a high aspect ratio tabular grain emulsion according to the present disclosure. The present disclosure is fully applicable to both additive multi-color imaging and subtractive multi-color imaging.

To illustrate the application of this disclosure to additive multi-color imaging, a filter array containing interlaid blue, green, and red filter elements can be employed in combination with a photographic element according to the present disclosure capable of producing a silver image. A high aspect ratio tabular grain emulsion of the present disclosure which is panchromatically sensitized and which forms a layer of the photographic element is imagewise exposed through the additive primary filter array. After processing to produce a silver image and viewing through the filter array, a multi-color image is seen. Such images are best viewed by projection. Hence both the photographic element and the filter array both have or share in common a transparent support.

Significant advantages can be realized by the application of this disclosure to multi-color photographic elements which produce multi-color images from combinations of subtractive primary imaging dyes. Such photographic elements are comprised of a support and typically at least a triad of superimposed silver halide emulsion layers for separately recording blue, green, and red exposures as yellow, magenta, and cyan dye images, respectively. Although the present disclosure generally embraces any multi-color photographic element of this type including at least one high aspect ratio tabular grain silver halide emulsion, additional advantages can be realized when high aspect ratio tabular grain silver bromide and bromoiodide emulsions are employed. Consequently, the following description is directed to certain preferred embodiments incorporating silver bromide and bromoiodide emulsions, but high aspect ratio tabular grain emulsions of any halide composition can be substituted, if desired. Except as specifically otherwise described, the multi-color photographic elements can incorporate the features of the photographic elements described previously.

In a specific preferred form of the disclosure a minus blue sensitized high aspect ratio tabular grain silver bromide or bromoiodide emulsion according to the disclosure forms at least one of the emulsion layers intended to record green or red light in a triad of blue, green, and red recording emulsion layers of a multi-color photographic element and is positioned to receive during exposure of the photographic element to neutral light at 5500°K blue light in addition to the light the emulsion is intended to record. The relationship of the blue and minus blue light the layer receives can be expressed in terms of log E, where

$$\log E = \log E_T - \log E_B$$

log E_T being the log of exposure to green or red light the tabular grain emulsion is intended to record and

log E_B being the log of concurrent exposure to blue light the tabular grain emulsion also receives. (In each occurrence exposure, E, is in meter-candle-seconds, unless otherwise indicated).

In the practice of the present disclosure log E can be less than 0.7 (preferably less than 0.3) while still obtaining acceptable image replication of a multi-color subject. This is surprising in view of the high proportion of grains present in the emulsions of the present disclosure having an average diameter of greater than 0.7 micron. If a comparable nontabular or lower aspect ratio tabular grain emulsion of like halide composition and average grain diameter is substituted for a high aspect ratio tabular grain silver bromide or bromoiodide emulsion of the present disclosure a higher and usually unacceptable level of color falsification will result. It is known in the art that color falsification by green or red sensitized silver bromide and bromoiodide emulsions can be reduced by reduction of average grain diameters, but this results in limiting maximum achievable photographic speeds as well. The present disclosure achieves not only advantageous separation in blue and minus blue speeds, but is able to achieve this advantage without any limitation on maximum realizable minus blue photographic speeds. In a specific preferred form of the disclosure at least the minus blue recording emulsion layers of

the triad of blue, green, and red recording emulsion layers are silver bromide or bromiodide emulsions according to the present disclosure. It is specifically contemplated that the blue recording emulsion layer of the triad can advantageously also be a high aspect ratio tabular grain emulsion according to the present disclosure. In a specific preferred form of the disclosure the tabular grains present in each of the emulsion layers of the triad having a thickness of less than 0.3 micron have an average grain diameter of at least 1.0 micron, preferably at least 2.0 microns. In a still further preferred form of the disclosure the multicolor photographic elements can be assigned an ISO speed index of at least 180.

The multicolor photographic elements of the disclosure need contain no yellow filter layer positioned between the exposure source and the high aspect ratio tabular grain green and/or red emulsion layers to protect these layers from blue light exposure, or the yellow filter layer, if present, can be reduced in density to less than any yellow filter layer density heretofore employed to protect from blue light exposure red or green recording emulsion layers of photographic elements intended to be exposed in daylight. In one specifically preferred form of the disclosure no blue recording emulsion layer is interposed between the green and/or red recording emulsion layers of the triad and the source of exposing radiation. Therefore the photographic element is substantially free of blue absorbing material between the green and/or red emulsion layers and incident exposing radiation. If, in this instance, a yellow filter layer is interposed between the green and/or red recording emulsion layers and incident exposing radiation, it accounts for all of the interposed blue density.

Although only one green or red recording high aspect ratio tabular grain silver bromide or bromiodide emulsion as described above is required, the multicolor photographic element contains at least three separate emulsions for recording blue, green, and red light, respectively. The emulsions other than the required high aspect ratio tabular grain green or red recording emulsion can be of any convenient conventional form. Various conventional emulsions are illustrated by *Research Disclosure*, Item 17643, cited above, Paragraph 1, Emulsion preparation and types, here incorporated by reference. In a preferred form of the disclosure all of the emulsion layers contain silver bromide or bromiodide grains. In a particularly preferred form of the disclosure at least one green recording emulsion layer and at least one red recording emulsion layer is comprised of a high aspect ratio tabular grain emulsion according to this disclosure. If more than one emulsion layer is provided to record in the green and/or red portion of the spectrum, it is preferred that at least the faster emulsion layer contain high aspect ratio tabular grain emulsion as described above. It is, of course, recognized that all of the blue, green, and red recording emulsion layers of the photographic element can advantageously be tabular as described above, if desired, although this is not required for the practice of this disclosure.

The present disclosure is fully applicable to multicolor photographic elements as described above in which the speed and contrast of the blue, green, and red recording emulsion layers vary widely. The relative blue insensitivity of green or red spectrally sensitized high aspect ratio tabular grain silver bromide or silver bromiodide emulsion layers employed in this disclosure allow green and/or red recording emulsion layers to be positioned at any location within a multicolor photographic element independently of the remaining emulsion layers and without taking any conventional precautions to prevent their exposure by blue light.

The present disclosure is particularly applicable to multicolor photographic elements intended to replicate colors accurately when exposed in daylight. Photographic elements of this type are characterized by producing blue, green, and red exposure records of substantially matched contrast and limited speed variation when exposed to a 5500°K (daylight) source. The term 'substantially matched contrast' as employed herein means that the blue, green, and red records differ in contrast by less than 20 (preferably less than 10) percent, based on the contrast of the blue record. The limited speed variation of the blue, green, and red records can be expressed as a speed variation ($\log E$) of less than 0.3 $\log E$, where the speed variation is the larger of the differences between the speed of the green or red record and the speed of the blue record.

Both contrast and log speed measurements necessary for determining these relationships of the photographic elements of the disclosure can be determined by exposing a photographic element at a color temperature of 5500°K through a spectrally nonselective step wedge, such as a carbon test object, and processing the photographic element, preferably under the processing conditions contemplated in use. By measuring the blue, green, and red densities of the photographic element to transmission of blue light of 435.8 nm in wavelength, green light of 546.1 nm in wavelength, and red light of 643.8 nm in wavelength, as described by American Standard PH2.1-1952, published by American National Standards Institute (ANSI), 1430 Broadway, New York, NY 10018, blue, green, and red characteristic curves can be plotted for the photographic element. If the photographic element has a reflective support rather than a transparent support, reflection densities can be substituted for transmission densities. From the blue, green,

and red characteristic curves speed and contrast can be ascertained by procedures well known to those skilled in the art. The specific speed and contrast measurement procedure followed is of little significance, provided each of the blue, green, and red records are identically measured for purposes of comparison. A variety of standard sensitometric measurement procedures for multicolor photographic elements intended for differing photographic applications have been published by ANSI. The following are representative: American Standard PH2.21-1979, PH2.47-1979, and PH2.27-1979.

The multicolor photographic elements of this disclosure capable of replicating accurately colors when exposed in daylight offer significant advantages over conventional photographic elements exhibiting these characteristics. In the photographic elements of the disclosure the limited blue sensitivity of the green and red spectrally sensitized tabular silver bromide or bromiodide emulsion layers can be relied upon to separate the blue speed of the blue recording emulsion layer and the blue speed of the minus blue recording emulsion layers. Depending upon the specific application, the use of tabular grains in the green and red recording emulsion layers can in and of itself provide a desirably large separation in the blue response of the blue and minus blue recording emulsion layers.

In some applications it may be desirable to increase further blue speed separations of blue and minus blue recording emulsion layers by employing conventional blue speed separation techniques to supplement the blue speed separations obtained by the presence of the high aspect ratio tabular grains. For example, if a photographic element places the fastest green recording emulsion layer nearest the exposing radiation source and the fastest blue recording emulsion layer farthest from the exposing radiation source, the separation of the blue speeds of the blue and green recording emulsion layers, though a full order of magnitude (1.0 $\log E$) different when the emulsions are separately coated and exposed, may be effectively reduced by the layer order arrangement, since the green recording emulsion layer receives all of the blue light during exposure, but the green recording emulsion layer and other overlying layers may absorb or reflect some of the blue light before it reaches the blue recording emulsion layer. In such circumstances employing a higher proportion of iodide in the blue recording emulsion layer can be relied upon to supplement the tabular grains in increasing the blue speed separation of the blue and minus blue recording emulsion layers. When a blue recording emulsion layer is nearer the exposing radiation source than the minus blue recording emulsion layer, a limited density yellow filter material coated between the blue and minus blue recording emulsion layers can be employed to increase blue and minus blue separation. In no instance, however, is it necessary to make use of any of these conventional speed separation techniques to the extent that they in themselves provide an order of magnitude difference in the blue speed separation or an approximation thereof, as has heretofore been required in the art (although this is not precluded if exceptionally large blue and minus blue speed separation is desired for a specific application). Thus, the present disclosure achieves the objectives for multicolor photographic elements intended to replicate accurately image colors when exposed under balanced lighting conditions while permitting a much wider choice in element construction than has heretofore been possible.

Multicolor photographic elements are often described in terms of color-forming layer units. Most commonly multicolor photographic elements contain three superimposed color-forming layer units each containing at least one silver halide emulsion layer capable of recording exposure to a different third of the spectrum and capable of producing a complementary subtractive primary dye image. Thus, blue, green, and red recording color-forming layer units are used to produce yellow, magenta, and cyan dye images, respectively. Dye imaging materials need not be present in any color-forming layer unit, but can be entirely supplied from processing solutions. When dye imaging materials are incorporated in the photographic element, they can be located in an emulsion layer or in a layer located to receive oxidized developing or electron transfer agent from an adjacent emulsion layer of the same color-forming layer unit.

To prevent migration of oxidized developing or electron transfer agents between color-forming layer units with resultant color degradation, it is common practice to employ scavengers. The scavengers can be located in the emulsion layers themselves, as taught by Yutzy et al US Patent 2,937,086 and/or in interlayers between adjacent color-forming layer units, as illustrated by Weissberger et al US Patent 2,336,327.

Although each color-forming layer unit can contain a single emulsion layer, two, three, or more emulsion layers differing in photographic speed are often incorporated in a single color-forming layer unit. Where the desired layer order arrangement does not permit multiple emulsion layers differing in speed to occur in a single color-forming layer unit, it is common practice to provide multiple (usually two or three) blue, green, and/or red recording color-forming layer units in a single photographic element.

It is a feature of this disclosure that at least one green or red

recording emulsion layer containing tabular silver bromide or bromiodide grains as described above is located in the multicolor photographic element to receive an increased proportion of blue light during imagewise exposure of the photographic element. The increased proportion of blue light reaching the high aspect ratio tabular grain emulsion layer can result from reduced blue light absorption by an overlying yellow filter layer or, preferably, elimination of overlying yellow filter layers entirely. The increased proportion of blue light reaching the high aspect ratio tabular emulsion layer can result also from repositioning the color-forming layer unit in which it is contained nearer to the source of exposing radiation. For example, green and red recording color-forming layer units containing green and red recording high aspect ratio tabular grain emulsions, respectively, can be positioned nearer to the source of exposing radiation than a blue recording color-forming layer unit.

The multicolor photographic elements of this disclosure can take any convenient form consistent with the requirements indicated above. Any of the six possible layer arrangements of Table 27a, p 211, disclosed by Gorokhovskii, *Spectral Studies of the Photographic Process*, Focal Press, New York, can be employed. To provide a simple, specific illustration, it is contemplated to add to a conventional multicolor silver halide photographic element during its preparation one or more high aspect ratio tabular grain emulsion layers sensitized to the minus blue portion of the spectrum and positioned to receive exposing radiation prior to the remaining emulsion layers. However, in most instances it is preferred to substitute one or more minus blue recording high aspect ratio tabular grain emulsion layers for conventional minus blue recording emulsion layers, optionally in combination with layer order arrangement modifications. The disclosure can be better appreciated by reference to the following preferred illustrative forms.

Layer Order Arrangement I

Exposure
+
B
IL
TG
IL
TR

Layer Order Arrangement II

Exposure
+
TFB
IL
TFG
IL
TFR
IL
SB
IL
SG
IL
SR

Layer Order Arrangement III

Exposure
+
TG
IL
TR
IL
B

Layer Order Arrangement IV

Exposure
+
TFG
IL
TFR
IL
TSG
IL
TSR
IL
B

Layer Order Arrangement V

Exposure
+
TFG
IL
TFR
IL
TFB
IL
TSG
IL
TSR
IL
SB

Layer Order Arrangement VI

Exposure
+
TFR
IL
TB
IL
TFG
IL
TFR
IL
SG
IL
SR

Layer Order Arrangement VII

Exposure
+
TFR
IL
TFG
IL
TB
IL
TFG

cont.

IL
TSG
IL
TFR
IL
TSR

Layer Order Arrangement VIII

Exposure
+
TFR
IL
FB
SB
IL + YF
FG
SG
IL
FR
SR

where

B, G, and R designate blue, green, and red recording color-forming layer units, respectively, of any conventional type;

T appearing before the color-forming layer unit B, G, or R indicates that the emulsion layer or layers contain a high aspect ratio tabular grain silver bromide or bromiodide emulsions, as more specifically described above,

F appearing before the color-forming layer unit B, G, or R indicates that the color-forming layer unit is faster in photographic speed than at least one other color-forming layer unit which records light exposure in the same third of the spectrum in the same Layer Order Arrangement;

S appearing before the color-forming layer unit B, G, or R indicates that the color-forming layer unit is slower in photographic speed than at least one other color-forming layer unit which records light exposure in the same third of the spectrum in the same Layer Order Arrangement; and

IL designates an interlayer containing a scavenger, but substantially free of yellow filter material. Each faster or slower color-forming layer unit can differ in photographic speed from another color-forming layer unit which records light exposure in the same third of the spectrum as a result of its position in the Layer Order Arrangement, its inherent speed properties, or a combination of both.

In Layer Order Arrangements I through VII, the location of the support is not shown. Following customary practice, the support will in most instances be positioned farthest from the source of exposing radiation — that is, beneath the layers as shown. If the support is colorless and specularly transmissive — i.e., transparent, it can be located between the exposure source and the indicated layers. Stated more generally, the support can be located between the exposure source and any color-forming layer unit intended to record light to which the support is transparent.

Turning first to Layer Order Arrangement I, it can be seen that the photographic element is substantially free of yellow filter material. However, following conventional practice for elements containing yellow filter material, the blue recording color-forming layer unit lies nearest the source of exposing radiation. In a simple form each color-forming layer unit is comprised of a single silver halide emulsion layer. In another form each color-forming layer unit can contain two, three, or more different silver halide emulsion layers. When a triad of emulsion layers, one of highest speed from each of the color-forming layer units, are compared, they are preferably substantially matched in contrast and the photographic speed of the green and red recording emulsion layers differ from the speed of the blue recording emulsion layer by less than 0.3 log E. When there are two, three, or more different emulsion layers differing in speed in each color-forming layer unit, there are preferably two, three, or more triads of emulsion layers in Layer Order Arrangement I having the stated contrast and speed relationship. The absence of yellow filter material beneath the blue recording color-forming unit increases the photographic speed of this layer.

It is not necessary that the interlayers be substantially free of yellow filter material in Layer Order Arrangement I. Less than conventional amounts of yellow filter material can be located between the blue and green recording color-forming units without

departing from the teachings of this disclosure. Further, the interlayer separating the green and red recording color-forming layer units can contain up to conventional amounts of yellow filter material without departing from the disclosure. Where conventional amounts of yellow filter materials are employed, the red recording color-forming unit is not restricted to the use of tabular silver bromide or bromiodide grains, as described above, but can take any conventional form, subject to the contrast and speed considerations indicated.

To avoid repetition, only features that distinguish Layer Order Arrangements II through VII from Layer Order Arrangement I are specifically discussed. In Layer Order Arrangement II, rather than incorporate faster and slower blue, red, or green recording emulsion layers in the same color-forming layer unit, two separate blue, green, and red recording color-forming layer units are provided. Only the emulsion layer or layers of the faster color-forming units need contain tabular silver bromide or bromiodide grains, as described above. The slower green and red recording color-forming layer units because of their slower speeds as well as the overlying faster blue recording color-forming layer unit, are adequately protected from blue light exposure without employing a yellow filter material. The use of high aspect ratio tabular grain silver bromide or bromiodide emulsions in the emulsion layer or layers of the slower green and/or red recording color-forming layer units is, of course, not precluded. In placing the faster red recording color-forming layer unit above the slower green recording color-forming layer unit, increased speed can be realized, as taught by Eccles et al US Patent 4,184,876, Ranz et al German OLS 2,704,797, and Lohman et al German OLS 2,622,923, 2,622,924, and 2,704,826.

Layer Order Arrangement III differs from Layer Order Arrangement I in placing the blue recording color-forming layer unit farthest from the exposure source. This then places the green recording color-forming layer unit nearest and the red recording color-forming layer unit nearer the exposure source. This arrangement is highly advantageous in producing sharp, high quality multi-color images. The green recording color-forming layer unit, which makes the most important visual contribution to multicolor imaging, as a result of being located nearest the exposure source is capable of producing a very sharp image, since there are no overlying layers to scatter light. The red recording color-forming layer unit, which makes the next most important visual contribution to the multicolor image, receives light that has passed through only the green recording color-forming layer unit and has therefore not been scattered in a blue recording color-forming layer unit. Though the blue recording color-forming layer unit suffers in comparison to Layer Order Arrangement I, the loss of sharpness does not offset the advantages realized in the green and red recording color-forming layer units, since the blue recording color-forming layer unit makes by far the least significant visual contribution to the multicolor image produced.

Layer Order Arrangement IV expands Layer Order Arrangement III to include separate faster and slower high aspect ratio tabular grain emulsion containing green and red recording color-forming layer units. Layer Order Arrangement V differs from Layer Order Arrangement IV in providing an additional blue recording color-forming layer unit above the slower green, red, and blue recording color-forming layer units. The faster blue recording color-forming layer unit employs high aspect ratio tabular grain silver bromide or bromiodide emulsion, as described above. The faster blue recording color-forming layer unit in this instance acts to absorb blue light and therefore reduces the proportion of blue light reaching the slower green and red recording color-forming layer units. In a variant form, the slower green and red recording color-forming layer units need not employ high aspect ratio tabular grain emulsions.

Layer Order Arrangement VI differs from Layer Order Arrangement IV in locating a tabular grain blue recording color-forming layer unit between the green and red recording color-forming layer units and the source of exposing radiation. As is pointed out above, the tabular grain blue recording color-forming layer unit can be comprised of one or more tabular grain blue recording emulsion layers and, where multiple blue recording emulsion layers are present, they can differ in speed. To compensate for the less favored position the red recording color-forming layer units would otherwise occupy, Layer Order Arrangement VI also differs from Layer Order Arrangement IV in providing a second fast red recording color-forming layer unit, which is positioned between the tabular grain blue recording color-forming layer unit and the source of exposing radiation. Because of the favored location which the second tabular grain fast red recording color-forming layer unit occupies it is faster than the first fast red recording layer unit if the two fast red-recording layer units incorporate identical emulsions. It is, of course, recognized that the first and second fast tabular grain red recording color-forming layer units can, if desired, be formed of the same or different emulsions and that their relative speeds can be adjusted by techniques well known to those skilled in the art. Instead of employing two fast red recording layer units, as shown, the second fast red recording layer unit can, if desired, be replaced with a second fast green

recording color-forming layer unit. Layer Order Arrangement VII can be identical to Layer Order Arrangement VI, but differs in providing both a second fast tabular grain red-recording color-forming layer unit and a second fast tabular grain green recording color-forming layer unit interposed between the exposing radiation source and the tabular grain blue recording color-forming layer unit.

Layer Order Arrangement VIII illustrates the addition of a high aspect ratio tabular grain red recording color-forming layer unit to a conventional multicolor photographic element. Tabular grain emulsion is coated to lie nearer the exposing radiation source than the blue recording color-forming layer units. Since the tabular grain emulsion is comparatively insensitive to blue light, the blue light striking the tabular grain emulsion does not unacceptably degrade the red record formed by the tabular grain red recording color-forming layer unit. The tabular grain emulsion can be faster than the silver halide emulsion present in the conventional fast red recording color-forming layer unit. The faster speed can be attributable to an intrinsically faster speed, the tabular grain emulsion being positioned to receive red light prior to the fast red recording color-forming layer unit in the conventional portion of the photographic element, or a combination of both. The yellow filter material in the interlayer beneath the blue recording color-forming layer units protects the conventional minus blue (green and red) color-forming layer units from blue exposure. Whereas in a conventional multicolor photographic element the red recording color-forming layer units are often farthest removed from the exposing radiation source and therefore tend to be slower and/or less sharp than the remaining color-forming layer units, in Arrangement VIII the red record receives a boost in both speed and sharpness from the additional tabular grain red recording color-forming layer unit. Instead of an additional tabular grain red recording color-forming layer unit, an additional tabular grain green recording color-forming unit can alternatively be added, or a combination of both tabular grain red and green recording color-forming layer units can be added. Although the conventional fast red recording layer unit is shown positioned beneath the slow green recording layer unit, it is appreciated that the relationship of these two units can be inverted, as illustrated in Layer Order Arrangement VI, for example.

There are, of course, many other advantageous layer order arrangements possible, Layer Order Arrangements I through VII being merely illustrative. In each of the various Layer Order Arrangements corresponding green and red recording color-forming layer units can be interchanged — ie, the faster red and green recording color-forming layer units can be interchanged in position in the various layer order arrangements and additionally or alternatively the slower green and red recording color-forming layer units can be interchanged in position.

Although photographic emulsions intended to form multicolor images comprised of combinations of subtractive primary dyes normally take the form of a plurality of superimposed layers containing incorporated dye-forming materials, such as dye-forming couplers, this is by no means required. Three color-forming components, normally referred to as packets, each containing a silver halide emulsion for recording light in one third of the visible spectrum and a coupler capable of forming a complementary subtractive primary dye, can be placed together in a single layer of a photographic element to produce multicolor images. Exemplary mixed packet multicolor photographic elements are disclosed by Godowsky US Patents 2,698,794 and 2,843,489. Although discussion is directed to the more common arrangement in which a single color-forming layer unit produces a single subtractive primary dye, relevance to mixed packet multicolor photographic elements will be readily apparent.

It is the relatively large separation in the blue and minus blue sensitivities of the green and red recording color-forming layer units containing tabular grain silver bromide or bromiodide emulsions that permits reduction or elimination of yellow filter materials and/or the employment of novel layer order arrangements. One technique that can be employed for providing a quantitative measure of the relative response of green and red recording color-forming layer units to blue light in multicolor photographic elements is to expose through a step tablet a sample of a multicolor photographic element according to this disclosure employing first a neutral exposure source — ie, light at 5500° K — and thereafter to process the sample. A second sample is then identically exposed, except for the interposition of a Wratten 98 filter, which transmits only light between 400 and 490 nm, and thereafter identically processed. Using blue, green, and red transmission densities determined according to American Standard PH2.1-1952, as described above, three dye characteristic curves can be plotted for each sample. The difference in blue speed of the blue recording color-forming layer unit(s) and the blue speed of the green or red recording color-forming layer unit(s) can be determined from the relationship:

$$(A) (BW98 - GW98) - (BN - GN) \text{ or}$$

$$(B) (BW98 - RW98) - (BN - RN)$$

where

BW98 is the blue speed of the blue recording color-forming layer unit(s) exposed through the Wratten 98 filter;

GW98 is the blue speed of the green recording color-forming layer unit(s) exposed through the Wratten 98 filter;

RW98 is the blue speed of the red recording color-forming layer unit(s) exposed through the Wratten 98 filter;

BN is the blue speed of the blue recording color-forming layer unit(s) exposed to neutral (5500° K) light;

GN is the green speed of the green recording color-forming layer unit(s) exposed to neutral (5500° K) light; and

RN is the red speed of the red recording color-forming layer unit(s) exposed to neutral (5500° K) light.

(The above description imputes blue, green, and red densities to the blue, green, and red recording color-forming layer units, respectively, ignoring unwanted spectral absorption by the yellow, magenta, and cyan dyes. Such unwanted spectral absorption is rarely of sufficient magnitude to affect materially the results obtained for the purposes they are here employed.)

The multicolor photographic elements of the present disclosure in the absence of any yellow filter material exhibit a blue speed by the blue recording color-forming layer units which is at least 6 times, preferably at least 8 times, and optimally at least 10 times the blue speed of green and/or red recording color-forming layer units containing high aspect ratio tabular grain emulsions, as described above. By way of comparison, an example below demonstrates that a conventional multicolor photographic element lacking yellow filter material exhibits a blue speed difference between the blue recording color-forming layer unit and the green recording color-forming layer unit(s) of less than 4 times (0.55 log E) as compared to nearly 10 times (0.95 log E) for a comparable multicolor photographic element according to the present disclosure. This comparison illustrates the advantageous reduction in blue speed of green recording color-forming layer units that can be achieved using high aspect ratio tabular grain silver bromide or bromiodide emulsions.

Another measure of the large separation in the blue and minus blue sensitivities of multi-color photographic elements of the present disclosure is to compare the green speed of a green recording color-forming layer unit or the red speed of a red recording color-forming layer unit to its blue speed. The same exposure and processing techniques described above are employed, except that the neutral light exposure is changed to a minus blue exposure by interposing a Wratten 9 filter, which transmits only light beyond 490 nm. The quantitative difference being determined is

$$(C) \quad GW9 - GW98 \text{ or}$$

$$(D) \quad RW9 - RW98$$

where

GW98 and RW98 are defined above;

GW9 is the green speed of the green recording color-forming layer unit(s) exposed through the Wratten 9 filter; and

RW9 is the red speed of the red recording color-forming layer unit(s) exposed through the Wratten 9 filter. (Again unwanted spectral absorption by the dyes is rarely material and is ignored.)

Red and green recording color-forming layer units containing tabular silver bromide or bromiodide emulsions, as described above, exhibit a difference between their speed in the blue region of the spectrum and their speed in the portion of the spectrum to which they are spectrally sensitized (ie, a difference in their blue and minus blue speeds) of at least 10 times (1.0 log E), preferably at least 20 times (1.3 log E). In an example below the difference is greater than 20 times (1.35 log E) while for the comparable conventional multicolor photographic element lacking yellow filter material this difference is less than 10 times (0.95 log E).

In comparing the quantitative relationships A to B and C to D for a single layer order arrangement, the results will not be identical, even if the green and red recording color-forming layer units are identical (except for their wavelengths of spectral sensitization). The reason is that in most instances the red recording color-forming layer unit(s) will be receiving light that has already passed through the corresponding green recording color-forming layer unit(s). However, if a second layer order arrangement is prepared which is identical to the first, except that the corresponding green and red recording color-forming layer units have been interchanged in position, then the red recording color-forming layer unit(s) of the second layer order arrangement should exhibit substantially identical values for relationships B and D that the green recording color-forming layer units of the first layer order arrangement exhibit for relationships A and C, respectively. Stated more succinctly, the mere choice of green spectral sensitization as opposed to red spectral sensitization does not significantly influence the values obtained by the above quantitative comparisons. Therefore, it is common practice not to differentiate green and red speeds in comparison to blue speed, but to refer to green and red speeds generically as minus blue speed.

The high aspect ratio tabular grain silver halide emulsions of the present disclosure are advantageous because of their reduced high angle light scattering as compared to nontabular and lower aspect ratio tabular grain emulsions. While not wishing to be bound by any particular theory to account for the reduced high angle scattering properties of high aspect ratio tabular grain emulsions according to the present disclosure, it is believed that the large flat major crystal faces presented by the high aspect ratio tabular grains as well as the orientation of the grains in the coating account for the improvements in sharpness observed. Specifically, it has been observed that the tabular grains present in a silver halide emulsion coating are substantially aligned with the planar support surface on which they lie. Thus, light directed perpendicular to the photographic element striking the emulsion layer tends to strike the tabular grains substantially perpendicular to one major crystal face. The thinness of tabular grains as well as their orientation when coated permits the high aspect ratio tabular grain emulsion layers of this disclosure to be substantially thinner than conventional emulsion coatings, which can also contribute to sharpness. However, the emulsion layers of this disclosure exhibit enhanced sharpness even when they are coated to the same thicknesses as conventional emulsion layers.

In a specific preferred form of the disclosure the high aspect ratio tabular grain emulsion layers exhibit a minimum average grain diameter of at least 1.0 micron, most preferably at least 2 microns. Both improved speed and sharpness are attainable as average grain diameters are increased. While maximum useful average grain diameters will vary with the graininess that can be tolerated for a specific imaging application, the maximum average grain diameters of high aspect ratio tabular grain emulsions according to the present disclosure are in all instances less than 30 microns, preferably less than 15 microns, and optimally no greater than 10 microns.

Although it is possible to obtain reduced high angle scattering with single layer coatings of high aspect ratio tabular grain emulsions according to the present disclosure, it does not follow that reduced high angle scattering is necessarily realized in multicolor coatings. In certain multicolor coating formats enhanced sharpness can be achieved with the high aspect ratio tabular grain emulsions of this disclosure, but in other multicolor coating formats the high aspect ratio tabular grain emulsions of this disclosure can actually degrade the sharpness of underlying emulsion layers.

Referring back to Layer Order Arrangement I, it can be seen that the blue recording emulsion layer lies nearest to the exposing radiation source while the underlying green recording emulsion layer is a tabular emulsion according to this disclosure. The green recording emulsion layer in turn overlies the red recording emulsion layer. If the blue recording emulsion layer contains grains having an average diameter in the range of from 0.2 to 0.6 micron, as is typical of many nontabular emulsions, it will exhibit maximum scattering of light passing through it to reach the green and red recording emulsion layers. Unfortunately, if light has already been scattered before it reaches the high aspect ratio tabular grain emulsion forming the green recording emulsion layer, the tabular grains can scatter the light passing through to the red recording emulsion layer to an even greater degree than a conventional emulsion. Thus, this particular choice of emulsions and layer arrangement results in the sharpness of the red recording emulsion layer being significantly degraded to an extent greater than would be the case if no emulsions according to this disclosure were present in the layer order arrangement.

In order to realize fully the sharpness advantages of the present disclosure in an emulsion layer that underlies a high aspect ratio tabular grain emulsion layer according to the present disclosure it is preferred that the tabular grain emulsion layer be positioned to receive light that is free of significant scattering (preferably positioned to receive substantially specularly transmitted light). Stated another way, in the photographic elements of this disclosure improvements in sharpness in emulsion layers underlying tabular grain emulsion layers are best realized only when the tabular grain emulsion layer does not itself underlie a turbid layer. For example, if a high aspect ratio tabular grain green recording emulsion layer overlies a red recording emulsion layer and underlies a Lippmann emulsion layer and/or a high aspect ratio tabular grain blue recording emulsion layer according to this disclosure, the sharpness of the red recording emulsion layer will be improved by the presence of the overlying tabular grain emulsion layer or layers. It is, of course, immaterial whether the red recording emulsion layer is itself a high aspect ratio tabular grain emulsion layer according to this disclosure insofar as the effect of the overlying layers on its sharpness is concerned.

In a multicolor photographic element containing superimposed color-forming units it is preferred that at least the emulsion layer lying nearest the source of exposing radiation be a high aspect ratio tabular grain emulsion in order to obtain the advantages of sharpness offered by this disclosure. In a specifically preferred form of the disclosure each emulsion layer which lies nearer the exposing radiation source than another image recording emulsion layer is a high aspect ratio tabular grain emulsion layer. Layer Order Arrange-

ments II, III, IV, V, VI, VII, and VIII, described above, are illustrative of multicolor photographic element layer arrangements according to the disclosure which are capable of imparting significant increases in sharpness to underlying emulsions layers.

Although the advantageous contribution of high aspect ratio tabular grain emulsions to image sharpness in multicolor photographic elements has been specifically described by reference to multicolor photographic elements, sharpness advantages can also be realized in multilayer black-and-white photographic elements intended to produce silver images. It is conventional practice to divide emulsions forming black-and-white images into faster and slower layers. By employing high aspect ratio tabular grain emulsions according to this disclosure in layers nearest the exposing radiation source the sharpness of underlying emulsion layers will be improved.

The disclosure is further illustrated by the following examples:

Examples to Illustrate Speed/Granularity Relationships

A series of silver bromide emulsions of varying aspect ratio as described below were prepared. The physical descriptions of the emulsions are given in Table I.

Chemical and spectral sensitization was optimum for the sensitizers employed.

TABLE I

PHYSICAL DESCRIPTIONS OF SILVER BROMIDE EMULSIONS 1-7

Emul- sion No.	Iodide Content (M/I)	Tabular Grain Diameter (μ m)	Thick- ness (μ m)	Aver- age Aspect Ratio	% of Pro- jected Area
1	6	3.8	0.14	27:1	>50
2	1.2	3.8	0.14	27:1	75
3	12.0	2.8	0.15	19:1	>90
4	12.3	1.8	0.12	15:1	>50
5	4.7	1.4	0.42	3.3:1	--
6	10	1.1	0.40	2.8:1	--
7	5	1.0	0.40	2.5:1	--

Emulsions 1 through 4 were high aspect ratio tabular grain emulsions within the definition of this disclosure. Although some tabular grains of less than 0.6 micron in diameter were included in computing the tabular grain average diameters and percent projected area in these and subsequent example emulsions, except where this exclusion is specifically noted, insufficient small diameter tabular grains were present to alter significantly the numbers reported.

To obtain a representative average aspect ratio for the grains of Emulsions 5 through 7 the average grain diameter was compared to the average grain thickness. Although not measured, the projected area that could be attributed to the few tabular grains meeting the less than 0.3 micron thickness and at least 0.6 micron diameter criteria was in each instance estimated by visual inspection to account for very little, if any, of the total projected area of the total grain population of the control emulsions.

B Speed/Granularity of Single Layer Incorporated Coupler Photographic Materials

The chemically and spectrally sensitized emulsions (Emulsion Nos 1-7) were separately coated in a single-layer magenta format on a cellulose triacetate film support. Each coated element comprised in addition to the silver halide emulsion, gelatin, a solvent dispersion of a magenta image-forming coupler, an antistain agent, a hardener, and an antifoggant, together with a gelatin overcoat layer.

The resulting photographic elements were exposed for 1/100 of a second through a 0-3.0 density step tablet plus a Wratten No 9 filter and 1.26 neutral density filter, to a 600W, 3000°K tungsten light source. Processing was accomplished at 37.7° C in a color process of the type described in the *British Journal of Photography Annual*, 1979, pp 204-206. The development times were varied to produce fog densities of about 0.10. The relative green sensitivity and the rms granularity were determined for each of the photographic elements. (The rms granularity is measured by the method described by H C Schmitt, Jr and J H Altman, *Applied Optics*, 9, pp 871-874, April 1970).

The optimally chemically and spectrally sensitized silver bromide emulsions having high aspect ratios exhibit a much better speed-granularity relationship than do the low aspect ratio silver bromide emulsions.

It should be noted that the use of a single-layer format, where all the silver halide emulsions are coated at equal silver coverage and with a common silver/coupler ratio, is the best format to illustrate the speed-granularity performance of a silver halide emulsion without introducing complicating interactions. For example, it is well known to those skilled in the photographic art that there are many methods of improving the speed-granularity

relationship of a color photographic element. Such methods include multiple-layer coating of the silver halide emulsion units sensitive to a given region of the visible spectrum. This technique allows control of granularity by controlling the silver/coupler ratio in each of the layers of the unit. Selecting couplers on the basis of reactivity is also known as a method of modifying granularity. The use of competing couplers, which react with oxidized color developer to either form a soluble dye or a colorless compound, is a technique often used. Another method of reducing granularity is the use of development inhibitor releasing couplers and compounds.

C Speed/Granularity of Black-and-White Photographic Materials

To illustrate speed/granularity advantage in black-and-white photographic materials five of the chemically and spectrally sensitized emulsions described above, Emulsions 1, 4, 5, 6, and 7, were coated on a poly(ethylene terephthalate) film support. Each coated element comprised silver halide emulsion and gelatin to which had been added antifoggant. An overcoat layer, comprising gelatin, was applied. The gelatin of the emulsion layer and overcoat was hardened.

The resulting photographic elements were exposed for 1/100 of a second through a 0-3.0 density step tablet plus a Wratten No 9 filter and a 1.26 neutral density filter, to a 600W, 3000° K tungsten light source. The exposed elements were then developed in an N-methyl-p-aminophenol sulfate-hydroquinone (Kodak DK-50®) developer at 20° C, the low aspect ratio emulsions were developed for 5 minutes while the high aspect ratio emulsions were developed for 3 1/2 minutes to achieve matched curve shape for the comparison. The speed-granularity relationship was superior for the high aspect ratio tabular grain emulsion of this disclosure.

Example Relating to Group VIII Noble Metal Doped Tabular Grain Emulsion

Emulsion A

An 0.8 μ m average grain size low aspect ratio (< 3:1) AgBrI (1 mole percent iodide) emulsion was prepared by a double-jet precipitation technique similar to that described in Illingsworth US Patent 3,320,069, and had 0.12 mg/silver mole ammonium hexachlororhodate(III) present during the formation of the silver halide crystals. The emulsion was then sulfur and gold sensitized. Following chemical sensitization, the emulsion was spectrally sensitized with a benzimidazoloxacarboquinone dye.

The low aspect ratio AgBrI emulsion was coated at 1.75 g/m² silver and 4.84 g/m² gelatin over a titanium dioxide gelatin (10:1) layer on a paper support. The emulsion layer contained 4.65 g/silver mole 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene. An overcoat was placed on the emulsion layer, consisting of 0.85 g/m² gelatin.

Emulsion B

The tabular grain silver bromoiodide (1 M% iodide) emulsion had an average tabular grain diameter of 1.5 μ m, an average tabular grain thickness of 0.08 μ m. The tabular grains exhibited an average aspect ratio of 19:1 and accounted for 90 percent of the projected area of the total grain population, measured as described above. The tabular grain emulsion was then sulfur and gold sensitized. Following chemical sensitization, the tabular grain emulsion was spectrally sensitized. The tabular grain emulsion, Emulsion B, was then coated in the same manner as described above for Emulsion A.

Exposure and Process

The two coatings described above were exposed on an Edgerton, Germeshausen, and Grier sensitometer at 10⁻⁴ sec using a graduated density step tablet and a 0.85 neutral density filter. The step tablet had 0-3.0 density with 0.15 density steps.

The exposed coatings were then developed in a hydroquinone-1-phenyl-3-pyrazolidone type black-and-white developer. Following fixing and washing, the coatings were submitted for densitometry.

The rhodium-doped AgBrI tabular grain emulsion coated at a lower silver coverage exhibited higher maximum density and was faster than the control. Contrast of the two coatings was nearly equivalent.

Examples Illustrating Increased Speed Separation of Spectrally Sensitized and Native Sensitivity Regions

Four multicolor photographic elements were prepared, herein-after referred to as Structures I through IV. Except for the differences specifically identified below, the elements were substantially identical in structure.

Structure I Exposure

↑
OC
B
IL + YF
FG
YL
FR
IL
SG
YL
SR

Structure II Exposure

↑
OC
B
IL
FG
YL
FR
IL
SG
YL
SR

Structure III Exposure

↑
OC
B
IL
TFG
YL
TFR
IL
SG
YL
SR

Structure IV Exposure

↑
OC
B
IL + YF
TFG
YL
TFR
IL
SG
YL
SR

OC is a protective gelatin overcoat, YF is yellow colloidal silver coated at 0.69 g/m² serving as a yellow filter material, and the remaining terms are as previously defined in connection with Layer Order Arrangements I through V. The blue (B), green (G), and red (R) recording color-forming layer units lacking the T prefix contained low aspect ratio silver bromoiodide emulsions prepared as taught by Illingsworth US Patent 3,320,069. Corresponding layers in the separate structures were of the same iodide content, except as noted.

The faster tabular grain green-sensitive emulsion layer contained a tabular grain silver bromoiodide emulsion which had an average tabular grain diameter of 5.0 μ m and an average tabular grain thickness of about 0.11 μ m. The tabular grains accounted for about 90 percent of the total grain projected area and exhibited an average aspect ratio of about 45:1, measured as described above. The faster green- and red-sensitive emulsion layer of Structures I and II contained 9 mole percent iodide while the faster tabular grain green- and red-sensitive emulsion layers of Structures III and IV contained 1.5 and 1.2 mole percent iodide, respectively.

The faster tabular grain green-sensitive emulsion was then optimally spectrally and chemically sensitized through the addition of sulfur and gold sensitizers and a green sensitizing dye.

The faster tabular grain red-sensitive emulsion layer contained a tabular grain silver bromoiodide emulsion prepared and optimally sensitized in a manner similar to the tabular grain green-sensitized silver bromoiodide emulsion described directly above, differing only in that red spectral sensitization was undertaken.

Other details relating to Structure I through IV will be readily apparent from Eeles et al US Patent 4,184,876.

Structures I through IV were identically neutrally exposed with a 600 watt 2850° K source at 1/100 second using a Daylight 5 filter and a 0 to 4 density step tablet having 0.20 density steps. Separate samples of Structures I through IV were exposed as described above, but with the additional interposition of a Wratten 98 filter to obtain blue exposures. Separate samples of Structures I through IV were exposed as described above, but with the additional interposition of a Wratten 9 filter to obtain minus blue exposures. All samples were identically processed using the C-41 Color Negative Process described in *British Journal of Photography Annual*, 1979, p 204. Development was for 3 minutes 15 seconds at 38° C. Yellow, magenta, and cyan characteristic curves were plotted for each sample. Curves from different samples were compared by matching minimum density levels — that is, by superimposing the minimum density portions of the curves.

Results are summarized in Table II.

Table II	Structures			
	I	III	IV	
Green Structure Differences	FG	FG	TFG	TFG
Red Structure Differences	FR	FR	TFR	TFR
Yellow Filter	Yes	No	No	Yes
Log E Blue/Minus Blue Speed Differences				
A	1.3	0.55	0.95	1.75
B	1.9	0.95	1.60	>2.40
C	1.8	0.95	1.35	2.25
D	2.5	1.55	2.20	>3.10

A is the difference in the log of the blue speed of the blue recording color-forming unit and the log of the blue speed of the green recording color-forming unit, as determined by Equation (A) above; $(BW98 - GW98) - (BN - GN)$;

B is the difference in the log of the blue speed of the blue recording color-forming unit and the log of the blue speed of the red recording color-forming unit, as determined by Equation (B) above; $(BW98 - RW98) - (BN - RN)$;

C is the difference in the log of the green speed of the green recording color-forming unit and the log of the blue speed of the green recording color-forming unit, as determined by Equation (C) above; $GW9 - GW98$; and

D is the difference in the log of the red speed of the red recording color-forming unit and the log of the blue speed of the red recording color-forming unit, as determined by Equation (D) above; $RW9 - RW98$.

In comparing Structures II and III, it can be seen that superior speed separations are obtained with Structure III employing tabular grains according to the present disclosure. Although Structure III did not attain the speed separations of Structure I, Structure III did not employ a yellow filter material and therefore did not encounter the disadvantages already discussed attendant to the use of such materials. Although Structure IV employed larger amounts of yellow filter material than necessary for use in the photographic elements of this disclosure, Structure IV does show that the speed separations of Structure III could be increased, if desired, by employing even small yellow filter densities.

A monochrome element was prepared by coating the faster green-sensitized tabular grain emulsion layer composition, described above, on a film support and overcoating with a gelatin protective layer. The blue to minus blue speed separation of the element was then determined using the exposure and processing techniques described above. The quantitative difference determined by Equation (C), $GW9 - GW98$, was 1.28 Log E. This illustrates that adequate blue to minus blue speed separation can be achieved according to the present disclosure when the high aspect ratio tabular grain minus blue recording emulsion layer lies nearest the exposing radiation source and is not protected by any overlying blue absorbing layer.

Examples Relating to Improved Image Sharpness in Multilayer Photographic Elements Containing Tabular Grain Emulsions

The following three examples illustrate the improved image sharpness which is achieved by the use of high aspect ratio tabular grain emulsions in photographic materials. In these examples the control elements utilize low aspect ratio silver bromide emulsions of the type described in Illingsworth US Patent 3,320,069. For the purpose of these examples the low aspect ratio emulsions will be identified as conventional emulsions, their physical properties being described in Table III.

Table III

Conventional Emulsion No.	Average Grain Diameter	Average Aspect Ratio
C1	1.1 μ m	3:1
C2	0.4-0.8 μ m	3:1
C3	0.8 μ m	3:1
C4	1.5 μ m	3:1
C5	0.4-0.5 μ m	3:1
C6	0.4-0.8 μ m	3:1

The physical descriptions of four tabular grain (high aspect ratio) silver bromide emulsions generally similar to those described in relation to speed/grainularity improvements are described in Table IV.

TABLE IV

Tabular Emulsion No.	Tabular Grain			Tabular Grain Percentage of Projected Area
	Average Diameter	Thickness	Average Aspect Ratio	
T1	7.0-8.0 μ m	$\approx 0.19 \mu$ m	35-45:1	≈ 65
T2	3.0 μ m	$\approx 0.07 \mu$ m	35-45:1	> 50
T3	2.4 μ m	$\approx 0.09 \mu$ m	25-30:1	> 70
T4	1.5-1.8 μ m	$\approx 0.06 \mu$ m	25-30:1	> 70

The silver bromide emulsions described above (C1-C6 and T1-T4) were then coated in a series of multilayer elements. The specific variations are shown in the tables containing the results. Although the emulsions were chemically and spectrally sensitized, sensitization is not essential to produce the sharpness results observed.

Common Structure A

Overcoat Layer	
Fast Blue-Sensitive, Yellow Dye-Forming Layer	
Slow Blue-Sensitive, Yellow Dye-Forming Layer	
Interlayer (Yellow Filter Layer)	
Fast Green-Sensitized, Magenta Dye-Forming Layer	
Interlayer	
Fast Red-Sensitized, Cyan Dye-Forming Layer	
Interlayer	
Slow Green-Sensitized, Magenta Dye-Forming Layer	
Interlayer	
Slow Red-Sensitized, Cyan Dye-Forming Layer	
/ / / / /	S U P P O R T / / / / /

Exposure and Process

The procedure for obtaining photographic Modulation Transfer Functions is described in *Journal of Applied Photographic Engineering*, 6 (1):1-8, 1980.

Modulation Transfer Functions for red light were obtained by exposing the multilayer coatings for 1/15 sec at 60 percent modulation using a Wratten 29 and an 0.7 neutral density filter. Green MTF's were obtained by exposing for 1/15 sec at 60 percent modulation in conjunction with a Wratten 99 filter.

Processing was through the C-41 Color Negative Process as described in *British Journal of Photography Annual 1979*, p 204. Development time was 3-1/4 min at 38°C (100°F). Following process, Cascaded Modulation Transfer (CMT) Acutance Ratings at 16 mm magnification were determined from the MTF curves.

Results

The composition of the control and experimental coatings along with CMT acutance values for red and green exposures are shown in Table V.

TABLE V

Sharpness of Conventional Emulsion Color Multilayers Versus Multilayers Containing Tabular Emulsions in Certain Layers

Coating No.	1	2	3	4	5	6
FY	C1	T-1	T-1	T-1	T-1	T-1
SY	C2	T-2	T-2	T-2	T-2	T-2
FM	C3	T-3	T-3	C3	T-2	T-2
FC	C4	C4	C4	C4	C4	T-2
SM	C5	T-4	C5	C5	C5	C5
SC	C6	C6	C6	C6	C6	C6
Red CMT Acutance	79.7	82.7	84.0	83.1	85.3	86.3
Δ CMT Units	---	+3.0	+4.3	+3.4	+5.6	+6.6
Green CMT Acutance	86.5	93.1	92.8	90.1	92.8	92.1
Δ CMT Units	---	+6.6	+6.3	+3.6	+6.3	+5.6

Sharpness was improved by the presence of high aspect ratio tabular grain emulsions.

Common Structure B

Overcoat Layer	
Fast Blue-Sensitive, Yellow Dye-Forming Layer	
Slow Blue-Sensitive, Yellow Dye-Forming Layer	
Interlayer (Yellow Filter Layer)	
Fast Green-Sensitized, Magenta Dye-Forming Layer	
Slow Green-Sensitized, Magenta Dye-Forming Layer	
Interlayer	
Fast Red-Sensitized, Cyan Dye-Forming Layer	
Slow Red-Sensitized, Cyan Dye-Forming Layer	
Interlayer	
/ / / / /	S U P P O R T / / / / /

After coating, the multicolor photographic elements of Common Structure B were exposed and processed according to the procedure described in the preceding example. The composition variations of the control and experimental coatings along with CMT acutance ratings are shown in Table VI.

TABLE VI

Sharpness Changes As a Function of Tabular Emulsions And Layer Arrangements In Multilayer Photographic Elements

Silver Halide Layer	1	2	3
FY	C1	T-1	T-1
SY	C2	T-2	T-2
FM	C3	T-3	C3
SM	C5	T-4	C5
FC	C4	C4	C4
SC	C6	C6	C6
Red CMT Acutance	80.0	83.9	82.8
Δ CMT Units	---	+3.9	+2.8
Green CMT Acutance	87.3	94.3	92.3
Δ CMT Units	---	+7.0	+5.0

The data presented in Table VI illustrates beneficial changes in sharpness in photographic materials which can be obtained through the use of tabular grain emulsions lying nearest the source of exposing radiation

Common Structure C

Fast Magenta	
Slow Magenta	
/ / / / /	S U P P O R T / / / / /

Two monochrome elements, A (Control) and B (Example), were prepared by coating fast and slow magenta layer formulations on a film support.

TABLE VII

Emulsions		Layer
Element A	Element B	
C3	T3	Fast Magenta
C5	T4	Slow Magenta

The monochrome elements were then evaluated for sharpness according to the method described for the previous examples, with the following results.

TABLE VIII

Element	CMT Acutance (16 mm)
A (Control)	93.9
B (Tabular Grain Emulsion)	97.3

Example Illustrating Reduced High-Angle Scattering by High Aspect Ratio Tabular Grain Emulsions

To provide a specific illustration of the reduced high-angle scattering of high aspect ratio tabular grain emulsions according to this disclosure as compared to nontabular emulsions of the same average grain volume, a quantitative angular light scattering detection procedure was employed. According to this procedure an emulsion sample is coated on a transparent film support and mounted horizontally with the emulsion face down immersed in a transparent liquid of substantially matched refraction index to minimize Fresnel reflections at the surfaces of the support and the emulsions. Light from a point source was directed to the coated sample from above perpendicular to the upper support surface. A hemispherical collector of light was positioned below the coated sample. The most intense light was received on the hemispherical collector at a point corresponding to the projection of the light path prior to contact with the coated sample. The projection path and the coated sample surface form a ninety degree angle of intersection. By drawing a line between the projection path and coated sample lower surface intersection and any other point on the hemispherical collector an angle of deflection θ from the projection path is defined as well as a scattering angle ϕ measured from the lower coated sample surface. The two angles θ and ϕ are complements. High angle scattering is measured by measuring the total light received by the hemispherical surface as a function of the angle ϕ .

The high aspect ratio tabular grain emulsion according to the present disclosure consisted essentially of dispersing medium and tabular grains having an average diameter of 5.7 microns and an average thickness of 0.22 micron. The tabular grains accounted for more than 90% of the total projected area of the grains present. The average grain volume was 5.61 cubic microns. A control nontabular emulsion was employed having an average grain volume of 5.57 cubic microns. (When resolved into spheres of the same volume — ie, equivalent spheres — both emulsions had nearly equal grain diameters). Both emulsions had a total transmittance of 90% when they were immersed in a liquid having a matching refractive index. Each emulsion was coated on a transparent support at a silver coverage of 1.08 g/m².

As more specifically set forth below in Table IX, lower percentages of total transmitted light were received over the detection surface areas subtended by ϕ up to values of ϕ of 84° with the high aspect ratio tabular grain emulsion of this disclosure as compared to the control emulsion of similar average grain volume. From Table IX it is also apparent that the collection angle for both emulsions was substantially below 6°. Thus neither emulsion would be considered a turbid emulsion in terms of its light scattering characteristics. When ϕ was 70° the emulsion of the present disclosure exhibited only half of the high angle scattering of the control emulsion.

TABLE IX

Percent of Transmitted Light Contained Within Angle Phi

ϕ	Tabular Emulsion (Example)	Nontabular Emulsion (Control)	Percent Reduction
30°	2%	6%	67%
50°	5%	15%	67%
70°	12%	24%	50%
80°	25%	33%	24%
84°	40%	40%	0%

Example Illustrating Blue Spectral Sensitization of A Tabular Grain Emulsion

A tabular grain silver bromiodide emulsion (3 M% iodide) had an average grain diameter of about 1.0 μ m, a average thickness of about 0.10 μ m, yielding an aspect ratio of about 10:1. The tabular grains accounted for greater than 85% of the total projected area of the silver halide grains present in the emulsion layer. The emulsion was sulfur and gold sensitized.

Coating 1 — A portion of the chemically sensitized

emulsion was coated on a cellulose triacetate film support. The emulsion coating was comprised of tabular silver bromide grains (1.08 g Ag/m²) and gelatin to which had been added a magenta dye-forming coupler, antistain agent, and antifoggant.

Coating 2 — A second portion of the tabular grain silver bromide emulsion was spectrally sensitized to blue light by the addition of a blue spectral sensitizing dye (λ max 490 nm). The spectrally sensitized emulsion was then constituted and coated as above.

The coatings were exposed for 1/25 second through a 0-3.0 density step tablet to a 500W 5400°K tungsten light source. Processing was for 3 minutes in a color developer of the type described in the *British Journal of Photography Annual*, 1979, Pages 204-206.

Coating 2 exhibited a photographic speed faster than Coating 1, showing an effective increase in speed attributable to blue sensitization.

Example Illustrating a High Aspect Ratio Tabular Grain Silver Chloride Emulsion

A high aspect ratio tabular grain silver chloride emulsion contained tabular silver chloride grains having average diameters of 4.0 to 4.5 microns, an average thickness of 0.28 micron, and an average aspect ratio of 15:1, which accounted for greater than 80 percent of the total projected area. The tabular grains appeared dodecahedral, suggesting the presence of {110} and {111} edges.

Example Illustrating Internal Latent Image Tabular Grain Emulsion

The tabular grain silver bromide core emulsion was employed to prepare the core-shell tabular grain emulsion having an average grain diameter of 2.8 μ m, an average thickness of 0.09 μ m, and an average aspect ratio of about 31:1.

The core emulsion was then sulfur and gold sensitized.

After shelling, the resultant internally sensitized tabular grain AgBr emulsion had an average grain diameter of 5.5 μ m, an average thickness of 0.14 μ m, and an average aspect ratio of approximately 40:1. The tabular grains accounted for 85% of the total projected area of the silver halide grains.

The emulsion was spectrally sensitized and then coated on a polyester film support at 2.15 g/m² silver and 10.4 g/m² gelatin. The coating was exposed for 1/100 second through a 0-4.0 continuous density wedge (plus Wratten 12 filter) to a 600W 5500°K tungsten light source and processed for 6 minutes at 20°C in a N-methyl-p-aminophenol sulfate (ⓂMetol)-hydroquinone developer containing potassium iodide. The resulting internal negative image displayed good discrimination.

In perhaps the simplest image transfer application, a high aspect ratio tabular grain silver halide emulsion as described above is substituted for the silver halide emulsion layer in a conventional silver image transfer photographic film unit. In addition to a conventional photographic support on which the tabular silver halide emulsion layer is located, the silver image transfer film unit preferably includes a silver receiving layer comprised of silver halide physical developing nuclei or other silver precipitating agents. To produce a transferred silver image the silver receiving and emulsion layers are juxtaposed, and a processing solution containing a silver halide solvent is released to contact the emulsion and receiving layers after imagewise exposure of the tabular grain emulsion layer.

A wide variety of nuclei or silver precipitating agents can be utilized in the receiving layers used in silver image transfer processes. Such nuclei are incorporated into conventional photographic organic hydrophilic colloid layers such as gelatin and polyvinyl alcohol layers and include such physical nuclei or chemical precipitants as (a) heavy metals, especially in colloidal form and salts of these metals, (b) salts, the anions of which form silver salts less soluble than the silver halide of the photographic emulsion to be processed, and (c) nondiffusible polymeric materials with functional groups capable of combining with and insolubilizing silver ions.

Typical useful silver precipitating agents include sulfides, selenides, polysulfides, polyselenides, thiourea and its derivatives, mercaptans, stannous halides, silver, gold, platinum, palladium, mercury, colloidal silver, aminoguanidine sulfate, aminoguanidine carbonate, arsenous oxide, sodium stannite, substituted hydrazines, xanthates, and the like. Poly(vinyl mercaptoacetate) is an example of a suitable nondiffusing polymeric silver precipitant. Heavy metal sulfides such as lead, silver, zinc, aluminum, cadmium and bismuth sulfides are useful, particularly the sulfides of lead and zinc alone or in an admixture or complex salts of these with thioacetamide, dithiooxamide, or dithiobiuret. The heavy metals and the noble metals particularly in colloidal form are especially effective. Other silver precipitating agents will occur to those skilled in the present art.

The processing solution can take the form of any conventional silver halide developer containing a silver halide solvent. Illustrative of silver halide solvent containing processing solutions useful in providing transferred silver image in combination with these photographic image transfer film units are those disclosed by Rott US

Patent 2,352,014, Land US Patents 2,543,181 and 2,861,885, Yackel et al US Patent 3,020,155, and Stewart et al US Patent 3,769,014, here incorporated by reference.

In silver image transfer film units the emulsion and receiving layers can be related in any convenient conventional manner. The emulsion layer or layers and the receiving layer can be located on the same support or different supports. When the receiving layer is coated on a separate support, the layer and the support, together with any additional layers present, are collectively termed a receiver. In a common preferred peel-apart format the emulsion layer bearing support is opaque and the receiver support is reflective (eg, white) or is provided with a reflective layer beneath the receiving layer. Exposure occurs before juxtaposing the receiver and emulsion layer for processing. In a common integral format both the receiver support and the emulsion layer support are transparent and a reflective (eg, white) background for viewing the silver image is provided by overcoating the receiving layer with a reflection pigment layer or incorporating the pigment in the processing solution. A preferred receiver also commonly includes a neutralizing layer (also referred to as a pH lowering or acid layer) for terminating development and at least one timing layer (also sometimes referred to as a spacer or 'inert' spacer layer). Neutralizing and timing layers can alternatively be located on the emulsion bearing support. The receiver and emulsion bearing supports are preferably integral — that is, joined during exposure, processing, and viewing, but in various formats they can be separate during exposure, viewing, and/or a portion of processing. Exemplary materials for use in the neutralizing and timing layers are described in *Research Disclosure*, Vol 123, July 1974, Item 13331, and Vol 135, Item 13525, July 1975. Details of reflective layers and support materials, including incorporated ultraviolet absorbers and optical brighteners, are disclosed in *Research Disclosure*, Vol 151, November 1976, Item 15162. Specifically preferred transparent support materials are poly(ethylene terephthalate) and cellulose esters. Preferred reflective supports are resin-coated paper supports.

In a preferred embodiment, the film units of this disclosure contains an alkaline processing composition and means for its containment and discharge within the film unit. A preferred means is a rupturable container (eg, pod) which is adapted to be positioned during processing of the film unit so that a compressive force applied to the container by pressure-applying members, such as found in a camera designed for in-camera processing, will effect a discharge of the container's contents within the film unit. However, other methods of introducing the alkaline processing composition can be employed. Processing alternatives are further illustrated by *Research Disclosure*, Item 17643, cited above, Paragraphs XXIII, C and G, here incorporated by reference.

The photographic image transfer film units of the disclosure can alternatively provide a transferred dye image. Except as noted, the features of dye image transfer film units can be identical to those of the silver image transfer film units discussed above and are not redescribed in detail.

A silver image transfer film unit can be converted to a dye image transfer film unit by replacing the silver receiving layer with a dye receiving layer and incorporating a dye-image-providing material in the silver halide emulsion layer or in an adjacent layer. Since silver halide is not normally transferred to the receiving layer of a dye image transfer film unit, silver halide solvent is not an essential component of the alkaline processing solution of a dye image transfer film unit.

It is possible to construct a dye image transfer film unit according to the present disclosure capable of producing a monochromatic transferred dye image by locating on a support a single dye-providing layer unit comprised of a tabular silver halide emulsion layer as described above and at least one dye-image-providing material in the emulsion layer itself or in an adjacent layer of the layer unit. In addition, the dye image transfer film unit is comprised of a dye receiving layer capable of mordanting or otherwise immobilizing dye migrating to it. To produce a transferred dye image the tabular emulsion layer is imagewise exposed and an alkaline processing solution is brought into contact with the emulsion layer with the dye receiving and emulsion layers juxtaposed. In a particularly advantageous application for monochromatic transferred dye images a combination of dye-image-providing materials is employed to provide a neutral transferred dye image. This image can be used to supplement the transferred silver image or to replace it entirely in providing a viewable black-and-white image. Of course, monochromatic transferred dye images of any hue can be produced, if desired.

Multicolor dye image transfer film units of this disclosure employ three dye-providing layer units: (1) a cyan-dye-providing layer unit comprised of a red-sensitive silver halide emulsion having associated therewith a cyan-dye-image-providing material, (2) a magenta-dye-providing layer unit comprised of a green-sensitive silver halide emulsion having associated therewith a magenta-dye-image-providing material, and (3) a yellow-dye-providing layer unit comprised of a blue-sensitive silver halide emulsion having associated therewith a yellow dye-image-providing material. Each of the dye-providing layer units can contain one, two, three, or more separate silver halide emulsion layers as well as the dye-image-

providing material, located in the emulsion layers or in one or more separate layers forming part of the dye-providing layer unit. Any one or combination of the emulsion layers can be high aspect ratio tabular grain silver halide emulsion layers as described above. In a preferred form of the disclosure at least the fastest emulsion layers in the cyan and magenta-dye-providing layer units are high aspect ratio tabular grain silver halide emulsions as described above. At least the fastest emulsion layer in the yellow-dye-image-providing layer unit is also preferably comprised of a high aspect ratio tabular grain silver halide emulsion as described above, but the use of other, conventional silver halide emulsions in the yellow-dye-providing layer unit together with high aspect ratio tabular grain silver halide emulsions in the cyan and magenta-dye-providing layer units is also specifically contemplated.

Depending upon the dye-image-providing material employed, it can be incorporated in the silver halide emulsion layer or in a separate layer associated with the emulsion layer. The dye-image-providing material can be any of a number known in the art, such as dye-forming couplers, dye developers, and redox dye-releasers, and the particular one employed will depend on the nature of the element or film unit and the type of image desired. Materials useful in diffusion transfer film units contain a dye moiety and a monitoring moiety. The monitoring moiety, in the presence of the alkaline processing solution and as a function of silver halide development, is responsible for a change in mobility of the dye moiety. These dye-image-providing materials can be initially mobile and rendered immobile as a function of silver halide development, as described in Rogers US Patent 2,983,606. Alternatively, they can be initially immobile and rendered mobile, in the presence of an alkaline processing solution, as a function of silver halide development. This latter class of materials include redox dye-releasing compounds. In such compounds, the monitoring group is a carrier from which the dye is released as a direct function of silver halide development or as an inverse function of silver halide development. Compounds which release dye as a direct function of silver halide development are referred to as negative-working release compounds, while compounds which release dye as an inverse function of silver halide development are referred to as positive-working release compounds.

A preferred class of positive-working release compounds are the nitrobenzene and quinone compounds described in Chasman et al US Patent 4,139,379. In these compounds the dye moiety is attached to an electrophilic cleavage group, such as a carbamate group, ortho to the nitro group or the quinone oxygen, and is released upon reduction of the compound by an electron donor compound contained in the element or the processing composition. In areas where the electron donor compound is consumed by developing silver halide, no dye moiety is released.

Other useful positive-working release compounds are the hydroquinones described in Fields et al US Patent 3,980,479 and the benzisoxazolone compounds described in Hinshaw et al US Patent 4,199,354.

A preferred class of negative-working release compounds are the ortho or para sulfonamidophenols and naphthols described in Fleckenstein US Patent 4,054,312, Koyama et al US Patent 4,055,428, and Fleckenstein et al US Patent 4,076,529. In these compounds the dye moiety is attached to a sulfonamido group which is ortho or para to the phenolic hydroxy group and is released by hydrolysis after oxidation of the sulfonamido compound during development.

Another preferred class of negative-working release compounds are ballasted dye-forming (chromogenic) or nondye-forming (non-chromogenic) couplers having a mobile dye attached to a coupling-off site. Upon coupling with an oxidized color developing agent, such as a *para*-phenylenediamine, the mobile dye is displaced so that it can transfer to a receiver. The use of such negative-working dye image providing compounds is illustrated by Whitmore et al US Patent 3,227,550, Whitmore US Patent 3,227,552, and Fujiwhara et al UK Patent 1,445,797, the disclosures of which are here incorporated by reference.

Since the silver halide emulsions employed in the image transfer film units of the present disclosure are negative-working, the use of negative-working release compounds will produce negative transferred dye images. In order to obtain a positive transferred dye image using negative-working release compounds, known image reversing film unit and processing variations can be employed, such as illustrated by Faul et al US Patent 3,998,637 and Morgan et al US Patent 4,258,117.

Further details regarding the above release compounds, the manner in which they function, and the procedures by which they can be prepared are contained in the patents referred to above, the disclosures of which are incorporated herein by reference.

Any material can be employed as the dye receiving layer in the film units of this disclosure as long as it will mordant or otherwise immobilize the dye which diffuses to it. The optimum material chosen will, of course, depend upon the specific dye or dyes to be mordanted. The dye receiving layer can also contain ultraviolet absorbers to protect the dye image from fading due to ultraviolet light, brighteners, and similar materials to protect or enhance the dye image. A polyvalent metal, preferably immobilized by association with a polymer, can be placed in or adjacent the

receiving layer to chelate the transferred image dye, as taught by Archie et al US Patent 4,239,849 and Myers et al US Patent 4,241,163. Useful dye receiving layers and materials for their fabrication are disclosed in *Research Disclosure* Item 15162 and Morgan et al US Patent 4,258,117.

The alkaline processing composition employed in the dye image transfer film units can be an aqueous solution of an alkaline material, such as an alkali metal hydroxide or carbonate (eg, sodium hydroxide or sodium carbonate) or an amine (eg, diethylamine). Preferably the alkaline composition has a pH in excess of 11. Suitable materials for use in such compositions are disclosed in *Research Disclosure*, Item 15162, cited above.

A developing agent is preferably contained in the alkaline processing composition, although it can be contained in a separate solution or process sheet, or it can be incorporated in any processing solution penetrable layer of the film unit. When the developing agent is separate from the alkaline processing composition, the alkaline composition serves to activate the developing agent and provide a medium in which the developing agent can contact and develop silver halide.

A variety of silver halide developing agents can be used in processing the film units of this disclosure. The choice of an optimum developing agent will depend on the type of film unit with which it is used and the particular dye image-providing material employed. Suitable developing agents can be selected from such compounds as hydroquinone, aminophenols (eg, N-methylamino-phenol), 1-phenyl-3-pyrazolidinone, 1-phenyl-4,4 dimethyl-3-pyrazolidinone, 1-phenyl-4-methyl-4-hydroxymethyl-3-pyrazolidinone, and N,N,N',N'-tetramethyl-p-phenylenediamine. The non-chromogenic developers in this list are preferred for use in dye transfer film units, since they have a reduced propensity to stain dye image-receiving layers. All of these same developing agents are also useful in the silver transfer film units.

One of the advantages of the present disclosure is the rapidity with which the transferred image becomes viewable. The rapid accessibility of the viewable transferred image is directly attributable to the presence of one or more high aspect ratio tabular grain silver halide emulsions as described herein. Without being bound by any particular theory, it is believed that the geometrical configuration of the tabular silver halide grains accounts for rapid access to the transferred images. In image transfer processes it is the imagewise variation in development of the silver halide grains as a function of their imagewise exposure which modulates the transferred image. In some systems, such as those employing negative-working release compounds, described above, silver halide development is directly related to transferred imaging materials. The faster the silver halide develops, the faster the imaging materials are made available for viewing. In other systems, such as the silver image transfer and dye image transfer systems employing positive-working release compounds, described above, silver halide development is or controls a competing reaction that retards transfer of image materials and accounts for minimum density in the viewed image. When silver halide development is accelerated, the mechanisms accounting for transferred imaging materials with which silver halide development is competing and thereby modulating can also be accelerated.

The use of tabular grains to reduce the time elapsed between the commencement of processing and obtaining a viewable transferred image — ie, access time — in no way precludes the use of other image transfer film unit features which are known to reduce access time. When the present disclosure is employed in combination with other features for reducing access time at least additive results can be normally expected. In addition, there are still other features unique to the image transfer film units of this disclosure which can contribute to reduced access time.

A second advantage attainable with the image transfer film units of the present disclosure is the reduced variance of the transferred image as a function of temperature. This reduced variance in the transferred image is a direct result of employing one or more tabular silver halide emulsion layers, as described above. Without being bound by any particular theory, it is believed that the tabular silver halide grains show less variation in their development rates as a function of temperature. In image transfer systems in which silver halide development is directly related to transferred imaging materials this reduced temperature dependence of tabular silver halide grains results directly in reduced variance in the viewed image. In systems relying also upon competing mechanisms for generation of the viewable image, reduced silver halide development variance as a function of temperature can reduce variance in the transferred image to the extent it is attributable to silver halide development variance and to the extent it complements temperature variances in the competing mechanisms employed in imaging.

It has been observed that the dye image transfer film units of the present disclosure exhibit substantially higher photographic speeds at lower silver coverages than comparable conventional dye image transfer film units. It is well known to those skilled in the art that silver coverages below a threshold level result in reduction of observed photographic speed as determined from a transferred dye image. While speed decreases when the silver coverages

of silver halide emulsions are reduced, the speed reduction is much more gradual when high aspect ratio tabular grain emulsions are employed, thereby allowing lower silver coverages.

Acceptable photographic speeds in conventional multicolor image transfer film units are commonly obtained by employing silver halide in each of the yellow, magenta, and cyan-dye-providing layer units at silver coverages of about 1000 mg/m² or higher. It is specifically contemplated to employ substantially lower silver coverages.

Layer Order Arrangements

The image transfer film units of this disclosure can employ any layer order arrangement heretofore known to be useful in image transfer film units having one or more radiation-sensitive silver halide emulsion layers. In addition, the distinctive properties of tabular silver halide emulsions make possible highly advantageous layer order arrangements not heretofore known to the art. The following specific layer order arrangements are merely illustrative, many other arrangements being additionally contemplated:

To avoid unnecessary repetition, discussion of each successive layer order arrangement is directed to features which are distinctive as compared to prior layer order arrangements. Stated another way, features and advantages shared by the layer order arrangements are fully discussed only in connection with the first layer order arrangement in which they appear. If a feature or advantage is not shared by a subsequently described layer order arrangement, this is specifically pointed out

Layer Order Arrangement I

A Laminate and Peel-Apart Silver
Image Transfer Film Unit

Reflective Support
Silver Receiving Layer
Imagewise Exposure
↓
Tabular Silver Halide Emulsion Layer
Support

Layer Order Arrangement I is illustrative of a conventional laminate and peel-apart silver image transfer film unit. Upon image-wise exposure, the negative-working tabular silver halide emulsion layer produces a developable latent image. The silver receiving layer containing precipitation nuclei is laminated and an alkaline processing composition, not shown, is released between the silver receiving layer and emulsion layer following exposure. Development of the tabular silver halide grains bearing latent image sites occurs upon contact with the alkaline processing composition. Silver halide solvent contained in the processing composition dissolves the silver halide grains which are not developed. The dissolved silver halide migrates to the silver receiving layer where physical development occurs. A positive transferred silver image is produced in the silver receiving layer. Processing is terminated by peeling the reflective support having the silver receiving layer coated thereon from the remainder of the image transfer film unit.

While the layer order arrangement is conventional and employs conventional materials except for the tabular silver halide emulsion layer, significantly superior results are obtainable. The access time required to produce a viewable silver image in the receiving layer is substantially reduced. It is believed that this can be attributed to distinct advantages offered by tabular silver halide grains. First, tabular silver halide grains employed in the image transfer film units of this disclosure develop at a faster rate than comparable nontabular silver halide grains. At least of equal importance is that tabular silver halide grains according to this disclosure can be dissolved at a substantially higher rate than comparable nontabular grains.

Although the two processing mechanisms of development and solubilization can entirely account for the more rapid image access in Layer Order Arrangement I, a third characteristic of tabular grain emulsions can also be used to further reduce image access times. While high aspect ratio tabular grain emulsion layers can be coated in the same layer thicknesses as conventional emulsions without departing from the teachings of this disclosure, it is preferred to reduce the thickness of the high aspect ratio tabular grain silver halide emulsion layers as compared to corresponding conventional silver halide emulsion layers. In conventional silver halide emulsions employed in image transfer the emulsion layer thickness is substantially greater than the average grain diameter calculated from the grain projected areas. Further, the thickness of the layer is large enough to accommodate not just the average grains, but the largest grains present. Thus, if the largest nontabular silver halide grains in a silver halide emulsion layer of an image transfer film unit exhibit an average diameter of from 1 to 2 microns, the emulsion layer will

be at least 1 to 2 microns in thickness and will usually be substantially greater in thickness. On the other hand, it is possible to employ tabular silver halide grains as defined herein having diameters based on average projected areas of 1 to 2 microns and often still larger while the thickness of the tabular grains is less than 0.5 or even 0.3 micron. Thus, in an exemplary emulsion in which the tabular grains have an average thickness of 0.1 micron with an average diameter of 1 to 2 microns, the silver halide emulsion layer thickness can easily be reduced substantially below 1 micron. The present high aspect ratio tabular grain emulsion layers are preferably less than 4 times the average thickness of the tabular grains and are optimally less than twice the average thickness of the tabular grains. Significant reductions in the thickness of the high aspect ratio tabular grain silver halide emulsion layers of the disclosure can contribute to reduction in image access times by reducing the lengths of diffusion paths. Further, reduction of the lengths of diffusion paths can also contribute to improvements in sharpness.

Layer Order Arrangement II

An Integral Silver Image Transfer
Film Unit View

↓
Transparent Support
Neutralizing Layer
Timing Layer
Silver Receiving Layer
Reflective Layer
Opaque Layer
Tabular Silver Halide Emulsion Layer
Alkaline Processing Composi-
tion + Opacifier
Transparent Support
↓
Imagewise Exposure

Layer Order Arrangement II is a conventional integral format silver image transfer film unit, differing from the art solely by the incorporation of the tabular silver halide emulsion layer. Layer Order Arrangement II combines all of the advantages provided by the tabular silver halide emulsion layer, discussed above in connection with Layer Order Arrangement I and additionally provides the art recognized advantages of an integral format. Because of the presence of an opacifier in the alkaline processing solution, it is necessary to place the alkaline processing solution in the location indicated after imagewise exposure. Once in place the opacifier prevents further exposure of the emulsion layer, as can occur, for example, when the image transfer film unit is removed from a camera. Processing is terminated by the timing and neutralizing layers.

Layer Order Arrangement III

An Integral Monochromatic Dye Image Transfer
Film Unit View

↓
Transparent Support
Dye Receiving Layer
Reflective Layer
Opaque Layer
Tabular Silver Halide Emulsion Layer
With Dye-Image Providing Material
Alkaline Processing Composi-
tion + Opacifier
Timing Layer
Neutralizing Layer
Transparent Support
↓
Imagewise Exposure

Initially the alkaline processing composition containing opacifier is not present in the location shown. Therefore, upon

imagewise exposure light strikes the tabular silver halide emulsion layer. This produces a latent image corresponding to light-struck areas of the emulsion layer. To initiate processing the alkaline processing composition is placed in the position shown. Usually, but not necessarily, the image transfer film unit is removed from the camera in which it is exposed immediately following placement of the alkaline processing composition and opacifier. The opacifier and opaque layer together prevent further exposure of the emulsion layer. Upon development, a mobile dye or dye precursor is released from the emulsion layer. When the dye-image-providing material is a positive-working release compound, it is released in initially unexposed areas of the emulsion layer; when the dye-image-providing material is a negative-working release compound, the converse is true. The mobile dye or dye precursor penetrates the opaque layer and the reflective layer and is mordanted or otherwise immobilized in the dye receiving layer to permit viewing through the uppermost transparent support. Processing is terminated by the timing and neutralizing layers.

It is possible to convert Layer Order Arrangements I and II to monochromatic dye image transfer film units by including a dye-image-providing material in the high aspect ratio tabular grain silver halide emulsion layers, substituting a dye receiving layer for the silver receiving layer, and employing an alkaline processing composition appropriate for dye image transfer. Thus, in terms of possible layer sequence, monochromatic transferred dye images could be readily obtained by modifying Layer Order Arrangements I and II. If these modifications were undertaken, Layer Order Arrangement III would still differ from Layer Order Arrangement II in the location of the timing and neutralizing layers. The positions of the timing and neutralizing layers in Layer Order Arrangements II and III are interchangeable. Although not specifically illustrated, it is possible to combine both silver and dye image transfer in a single image transfer film unit, since the two are compatible. A useful application of such a combined image transfer film unit arises where the silver density is being supplemented by dye, allowing low silver coverages to be realized. Except for combined silver and dye imaging, dissolving of undeveloped silver halide is not normally undertaken in Layer Order Arrangement III and is not needed to obtain reduced transferred image access times. The presence of dye-image-providing material in the high aspect ratio tabular grain silver halide emulsion layer can significantly increase the thickness of this layer. As has been previously discussed, it is recognized that silver halide coverages can be significantly reduced in the high aspect ratio tabular grain silver halide emulsion layer while retaining acceptable photographic speed levels in dye image transfer film units. Layer Order Arrangement III is capable of providing this advantage.

Layer Order Arrangement IV

An Integral Multicolor Dye Image Transfer Film Unit
Imagewise Exposure

↓
<u>Transparent Support</u>
<u>Neutralizing Layer</u>
<u>Timing Layer</u>
<u>Alkaline Processing Composition + Opacifier</u>
<u>Transparent Overcoat</u>
<u>Blue-sensitive Tabular Silver Halide Emulsion Layer</u>
<u>Yellow Dye-Image-Providing Material Layer</u>
<u>Interlayer With Scavenger</u>
<u>Green-sensitive Tabular Silver Halide Emulsion Layer</u>
<u>Magenta Dye-Image-Providing Material Layer</u>
<u>Interlayer With Scavenger</u>
<u>Red-sensitive Tabular Silver Halide Emulsion Layer</u>
<u>Cyan Dye-Image-Providing Material Layer</u>
<u>Opaque Layer</u>
<u>Reflective Layer</u>
<u>Dye Receiving Layer</u>
<u>Transparent Support</u>

↑
View

Layer Order Arrangement IV is essentially similar to Layer Order Arrangement III, but is modified to contain three separate dye-providing layer units, each comprised of one high aspect ratio tabular grain silver halide emulsion layer and one dye-image-providing material layer, instead of the single dye-image-providing material containing high aspect ratio tabular grain silver halide emulsion layer of Layer Order Arrangement III. (Whether or not the dye-image-providing material is placed in the emulsion layer itself or in an adjacent layer in Layer Order Arrangements III and IV is a matter of choice, either arrangement being feasible).

To prevent color contamination of adjacent dye-providing layer units, an interlayer containing a scavenger is positioned between dye-providing layer units. The use of scavengers in interlayers is taught by Weissberger et al US Patent 2,336,327 and in the dye-providing layer units themselves by Yutzy et al US Patent 2,937,086. The use of scavengers in either or both locations is contemplated.

In a modification of Layer Order Arrangement IV it is possible to eliminate the interlayers. Since the high aspect ratio tabular grain silver halide emulsion layers can be quite thin in comparison to conventional silver halide emulsion layers typically employed in multicolor dye image transfer film units, each high aspect ratio tabular grain silver halide emulsion layer can be coated between two magenta dye-image-providing material layers. The two magenta-dye-image providing material layers preferably do not contain scavenger but can contain scavenger, if desired, depending upon the sensitivity of the imaging application to color contamination and the specific choice of dye-image-providing materials. Providing dye-image-providing layers adjacent both sides of each high aspect ratio tabular grain silver halide emulsion layer provides a close association between the dye-image-providing materials and the silver halide. This arrangement is most advantageous where the dye-image-providing materials of each dye-providing layer unit is initially colorless or at least shifted in hue so that the dye-image-providing material is not adsorbing in the spectral region to which the silver halide is intended to respond.

Where the yellow dye-image-providing material is initially yellow, it acts, together with the blue-sensitive high aspect ratio tabular grain silver halide emulsion layer, to intercept blue light that would otherwise reach the green and red-sensitive high aspect ratio tabular grain silver halide emulsion layers. Where the green and red-sensitive silver halide emulsion layers employ silver bromide or silver bromoiodide grains in a conventional multicolor dye image transfer film unit, it is necessary to intercept blue light to avoid color contamination of the green and red-sensitive emulsion layers. However, where the green and red-sensitive emulsions are high aspect ratio tabular grain, it is unnecessary to filter blue light so that it is attenuated before reaching these emulsion layers. Thus, where the yellow dye-image-providing material is initially colorless or at least nonabsorbing in the blue region of the spectrum, it is still possible for accurate color reproduction to occur in the magenta and cyan dye-providing layer units without any necessity of interposing a yellow filter layer. Further, as is more fully described below, the dye-providing color-forming layer units can be located in any desired order.

Layer Order Arrangement V

An Integral Multicolor Dye Image Transfer Film Unit

↓
<u>Opaque Support</u>
<u>Yellow Dye-Image-Providing Material Layer</u>
<u>Blue-sensitive Tabular Silver Halide Emulsion Layer</u>
<u>Interlayer With Scavenger</u>
<u>Cyan Dye-Image-Providing Material Layer</u>
<u>Red-sensitive Tabular Silver Halide Emulsion Layer</u>
<u>Interlayer With Scavenger</u>
<u>Magenta Dye-Image-Providing Material Layer</u>
<u>Green-sensitive Tabular Silver Halide Emulsion Layer</u>
<u>Transparent Overcoat</u>
<u>Alkaline Processing Composition With Reflective Material and Indicator Dye</u>
<u>Dye Receiving Layer</u>

Timing Layer
Neutralizing Layer
Transparent Support

↑
View and Imagewise Exposure

In Layer Order Arrangement V during imagewise exposure the alkaline processing composition containing the reflective material and indicator dye is not in the position shown, but is released to the position shown after exposure to permit processing. The indicator dye exhibits a high density at the elevated levels of pH under which processing occurs. It thereby protects the silver halide emulsion layers from further exposure if the film unit is removed from a camera during processing. Once the neutralizing layer reduces the pH within the film unit to terminate processing, the indicator dye reverts to an essentially colorless form. The alkaline processing composition also contains a reflective material, which provides a background for viewing the transferred dye image after processing.

Layer Order Arrangement V is illustrative of the application of the disclosure to an integral multicolor dye image transfer film unit format in which imagewise exposure and viewing occur through the same support. Layer Order Arrangement V differs from the prior teachings of the art not only in the use of high aspect ratio tabular grain silver halide emulsions, but also in the order in which the dye-providing layer units are arranged. The green-sensitive high aspect ratio tabular grain silver halide emulsion layer is nearest to the exposing radiation source while the blue-sensitive high aspect ratio tabular grain silver halide emulsion layer is farthest removed. This arrangement is possible without color contamination because of the relatively large separations in blue and minus blue response attainable with minus blue spectrally sensitized high aspect ratio tabular grain silver halide emulsions. By placing the magenta-dye-providing layer unit nearest the source of exposing radiation and nearest the dye receiving layer, the sharpness of the magenta dye image is improved and its access time is reduced. The magenta dye image is, of course, the visually most important component of the multicolor dye image. The cyan image is the visually second most important, and its location is also nearer the exposing radiation source and the dye receiving layer than in a corresponding conventional dye image transfer film unit. Thus, significant advantages in terms of reduced image access time and increased image sharpness are attainable with Layer Order Arrangement V in addition to those improvements attributable to high aspect ratio tabular grain silver halide grains previously discussed above in connection with other layer order arrangements. While Layer Order Arrangement V is useful with all high aspect ratio tabular grain silver halides, it is particularly advantageous with high aspect ratio tabular grain silver bromide or bromoiodide.

Layer Order Arrangement VI
An Integral Multicolor Dye Image Transfer
Film Unit With Image Reversal
Expose

↑

Transparent Support
Neutralizing Layer
Timing Layer
Alkaline Processing Composition + Opacifier
Green-sensitive Tabular Silver
Halide Emulsion Layer
Interlayer With Scavenger
Magenta Dye-Image-Providing Material
and Nuclei
Interlayer With Scavenger and Nuclei
Red-sensitive Tabular Silver
Halide Emulsion Layer
Interlayer With Scavenger
Cyan Dye-Image-Providing Material
and Nuclei
Interlayer With Scavenger and Nuclei
Blue-sensitive Tabular Silver
Halide Emulsion Layer

Interlayer With Scavenger
Yellow Dye-Image-Providing Material
and Nuclei
Opaque Layer
Reflective Layer
Dye Receiving Layer
Transparent Support

↑
View

During imagewise exposure of Layer Order Arrangement VI the alkaline processing composition containing the opacifier is not in the location shown. The alkaline processing composition is placed in the position shown to commence processing. Initially each of the high aspect ratio tabular grain silver halide emulsion layers develop in the areas which are light-struck during exposure. The emulsion layers each contain a scavenger to prevent any interaction of the oxidized developing agent produced by development of the light-struck silver halide and the dye-image-providing materials. A scavenger containing interlayer is also positioned between each high aspect ratio tabular grain silver halide emulsion layer and its corresponding dye-image-providing material layer for this purpose.

In the areas of the high aspect ratio tabular grain silver halide emulsion layers in which silver halide development does not occur, silver halide is solubilized by silver halide solvent contained in the alkaline processing composition. The solubilized silver halide migrates through the adjacent interlayer containing scavenger and is converted to silver on the nuclei present in the layer containing the dye-image-providing material. The nuclei can be those employed for physical development in silver image transfer. The oxidized developing agent produced as a result of physical development is free to react with the dye-image-providing material to release a mobile dye or dye precursor. Color contamination between adjacent dye-providing layer units is prevented by interposing therebetween a layer containing a scavenger to prevent the migration of oxidized developing agent therethrough and nuclei to prevent the migration of solubilized silver halide therethrough.

Layer Order Arrangement VI is illustrative of an integral multicolor dye image transfer film unit which produces a positive transferred dye image using negative-working silver halide emulsions and negative-working release compounds materials. Although the basic approach has been previously disclosed in the art, as illustrated by UK Patent 904,364, there are unexpected advantages to employing high aspect ratio tabular grain silver halide emulsions as herein described. It is to be noted that both the development and solubilizing of silver halide is required to obtain a transferred dye image. Because of the increased rates of development and solubilizing possible with high aspect ratio tabular grain silver halide emulsions, it is possible to reduce transferred image access times below those that have been previously obtained with the type of image reversal arrangement. Layer Order Arrangement VI also exhibits advantages attributable to a dye-providing layer unit arrangement similar to those already described in connection with Layer Order Arrangement V.

Although the disclosure has been particularly described with reference to certain preferred layer order arrangements, it is appreciated that the high aspect ratio tabular grain silver halide emulsions need not always be present as planar, uninterrupted layers. Rather than being continuous, the layers can be subdivided into discrete laterally displaced portions or segments. In multicolor image transfer film units the layers need not be superimposed, but can be present in the form of interlaid layer segments. It is specifically contemplated to employ high aspect ratio tabular grain silver halide emulsions as herein disclosed in microcellular image transfer film unit arrangements, such as disclosed by Whitmore Patent Cooperation Treaty published application W080/01614, published August 7, 1980, here incorporated by reference.

Although all of the advantages attributable to high aspect ratio tabular grain silver halide emulsions can be realized in microcellular image transfer film units, the large minus blue and blue speed separations obtainable with spectrally sensitized high aspect ratio tabular grain silver halide emulsions, most notably silver bromide and bromoiodide emulsions, are particularly advantageous in microcellular image transfer film units intended to produce multicolor images. Since the microcell triads intended to respond to blue, green, and red light are positioned to receive the same incident light, yellow filters are interposed using conventional silver bromide and bromoiodide emulsions to improve minus blue and blue speed separation. This can involve an additional coating or cell filling step and reduce photographic speed. The high aspect ratio tabular grain silver halide emulsions can be employed in multicolor microcellular image transfer film units without the use of yellow filters, thereby significantly simplifying

construction and improving performance.

Image Transfer Examples

The disclosure can be better appreciated by reference to the following illustrative examples.

Example 1

Control Emulsion A-1

A conventional low aspect ratio silver bromide control emulsion having an average grain diameter of 1.1 microns and containing 9 mole percent iodide was prepared as described in Illingsworth US Patent 3,320,069. The emulsion was optimally sensitized with sulfur and gold in the presence of thiocyanate and spectrally sensitized to green light using a supersensitizing combination of carbocyanine dyes.

Tabular Grain Emulsion B

A high aspect ratio tabular grain silver bromide emulsion containing tabular silver bromide grains having an average grain diameter of 4 microns, an average grain thickness of 0.13 micron, and an average aspect ratio of approximately 30:1 was prepared. The tabular silver bromide grains accounted for approximately 90 percent of the total grain projected area. The emulsion was optimally sensitized chemically with sulfur and gold in the presence of thiocyanate and spectrally sensitized with the same supersensitizing dye combination employed in Control Emulsion A-1.

Dye Image Transfer Film Units

Control Emulsion A-1 was coated on a support having an antihalation layer in a decreasing silver coverage series (1.38, 0.69, 0.53, and 0.36 g/m²) along with the materials shown below:

	Coverage
Redox Dye-Releaser	0.69 g/m ²
Incorporated Reducing Agent	0.42 g/m ²
Incorporated Phenylmercapto-tetrazole Antifoggant	0.009 g/m ²
4-Hydroxy-6-methyl-1,3,3a,7-tetraazaindene	1.2 g/Ag mole
Gelatin	1.1 g/m ²

In addition to the gelatin shown in the above table, for each gram of silver coated, an equal weight of gelatin was also present in the coating.

Tabular Grain Emulsion B of the disclosure was coated on a clear cellulose acetate support in a decreasing silver coverage series (1.35, 0.67, and 0.40 g/m²) along with the materials shown below:

	Coverage
Redox Dye-Releaser	0.80 g/m ²
Incorporated Reducing Agent	0.37 g/m ²
Incorporated Phenylmercapto-tetrazole Antifoggant	0.009 g/m ²
4-Hydroxy-6-methyl-1,3,3a,7-tetraazaindene	3.6 g/Ag mole
Gelatin	1.2 g/m ²

In addition to the gelatin shown in the above table, for each gram of silver coated, an equal weight of gelatin was also present in the coating.

Dye Image Receiver

The dye image receiver consisted of the following structure. Coverages are shown parenthetically in g/m².

- 6 Hydroxyethylcellulose layer (Natsol 250L) (0.97)
- 5 Gelatin layer (1.1)
- 4 Opaque layer: Carbon (1.9), Gelatin (1.1)
- 3 Reflecting layer: Titanium dioxide (19), Gelatin (3.0)
- 2 Mordant layer: Poly(4-vinylpyridine) (2.2), Gelatin (2.2)
- 1 Metal-containing layer: Nickel sulfate hexahydrate (0.58), gelatin (1.1)

Coated on clear polyester support in the order of numbering.

Exposure and Processing

The dye image transfer film units described above were exposed for 1/100 second to a 600 watt 2850°K tungsten light source through a step-chart, a 1.0 neutral density filter and a Wratten 16 filter.

The dye image transfer film units were processed by releasing processing fluid from a pod to the interface of the dye receiver and the emulsion layer by laminating between stainless steel rollers providing a 75 micron developer layer thickness. The processing

composition for Control Emulsion A-1 (Pod L) is shown below in Example 2. The composition of the pod for Tabular Grain Emulsion B was identical to Pod L, except it contained 16 grams/liter of the 3-pyrazolidinone electron transfer agent rather than 8 grams/liter.

In both instances transfers were carried out for 10 minutes at room temperature. The receivers were separated and the Status A green density was read. Characteristic curves were plotted, and relative speeds were determined at 0.2 density units below maximum density.

The sensitometric results obtained are shown below. Of particular interest are the relative threshold speeds at decreasing silver coverages for the two emulsions. The tabular grain emulsion coating maintained significantly higher relative speeds as the silver coverage was reduced compared to the conventional three-dimensional emulsion coating.

Coating/Ag Coverage	D _{max}	D _{min}	Contrast	Relative Speed*
Control Emulsion A-1				
1.38 g/m ²	1.74	0.16	1.7	100
0.69 g/m ²	2.04	0.17	2.2	59
0.53 g/m ²	2.11	0.13	2.4	51
0.36 g/m ²	2.16	0.17	2.3	24
Tabular Grain Emulsion B				
1.35 g/m ²	1.04	0.12	1.2	100
0.67 g/m ²	1.44	0.12	1.8	90
0.40 g/m ²	1.77	0.10	2.1	88

* 30 = 0.3 log E.

Example 2

Control Emulsion A-2

A conventional low aspect ratio polydisperse silver bromide emulsion containing some large grains up to about 2 microns and containing 6.2 mole percent iodide was prepared as described in Illingsworth US Patent 3,320,069. The emulsion was optimally chemically sensitized with sulfur and gold in the presence of thiocyanate and spectrally sensitized to green light using the same sensitizers employed with the tabular grain emulsion, Tabular Grain Emulsion C, described below.

Tabular Grain Emulsion C

A high aspect ratio tabular silver bromide emulsion having an average grain diameter of 4.7 microns, an average grain thickness of 0.16 micron, and an average aspect ratio of 29:1 was prepared. The tabular silver bromide grains accounted for greater than 95 percent of the total projected grain area. The emulsion was optimally sensitized chemically with sulfur and gold in the presence of thiocyanate and spectrally sensitized to green light using a supersensitizing combination of carbocyanine dyes.

Dye Image Transfer Film Units

Integral imaging receivers (IIR's) using the above emulsions of the following structure were prepared. Coverages are in (g/m²) unless otherwise specified.

- 7 Hydroxyethylcellulose (Natsol 250L) overcoat layer (0.54)
- 6 Magenta imaging layer: Green-sensitized negative silver halide Tabular Grain Emulsion C (0.74 Ag), Redox Dye-Releaser (0.67), Reducing Agent (0.36), Phenylmercapto tetrazole + PMT Inhibitor (0.009), 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene TAI Antifoggant (3.5 g/Ag mole), gelatin (1.7)
- 5 Gelatin interlayer (1.2)
- 4 Opaque layer: Carbon (1.9), gelatin (1.2)
- 3 Reflecting layer: Titanium dioxide (16.0), gelatin (2.6)
- 2 Mordant layer: Poly(4-vinylpyridine) (2.2), gelatin (2.2)
- 1 Metal-containing layer: Nickel sulfate hexahydrate (0.58), gelatin (1.1)

Coated on clear polyester support in the order of numbering.

A control was the same as the example coating described above, except Control Emulsion A-2 was used at 1.48 g Ag/m². Both coatings were hardened with bis(vinylsulfonyl)-methane at 1.1 percent of the gelatin weight.

Cover sheets of the following structure were prepared:

- 2 Timing layer: 1:1 physical mixture of the following two polymers coated at 4.8 g/m²: Poly(acrylonitrile-co-vinylidene chloride-co-acrylic acid) at a 14:79:7 weight ratio. The carboxy ester lactone formed by cyclization of a vinyl acetate-maleic anhydride copolymer in the presence of 1-butanol to produce a partial butyl ester of acid:ester of 15:85

- 1 Acid layer: Poly(n-butyl acrylate-co-acrylic acid) at a 30:70 weight ratio equivalent to 140 meq acid/m²

Coated on clear polyester support in the order numbered.

Processing pods of the following two compositions were prepared:

	Pod L	Pod M
Potassium hydroxide	60 g/l	60 g/l
4-Hydroxymethyl-4-methyl-1-phenyl-3-pyrazolidinone	8 g/l	6 g/l
Potassium bromide	5 g/l	10 g/l
Sodium sulfite	2 g/l	2 g/l
Carboxymethylcellulose	57 g/l	57 g/l

Exposure and Processing

Each integral imaging receiver (IIR) was exposed in a sensitometer to yield a full-scale D_{min}/D_{max} image after processing with a viscous processing composition in a pod. The processing composition was spread between the IIR and the cover sheet using a pair of rollers which provide a 100 μm gap. Within 12 to 24 hours the Status A green density of the receiver side of the IIR was read to obtain the sensitometric curves. The sensitometric parameters, D_{max}, D_{min}, contrast, and relative speed (at D = 0.3 below D_{max}) were read from the curves.

As the data below shows, the Tabular Grain Emulsion C, with either pod L, or the less active M pod, produced a relative speed that was 0.2 log E faster than the control emulsion processed with the same pod, despite the much lower silver coverage (0.74 g Ag/m² versus 1.48 g Ag/m²) of the tabular grain emulsion. The speed difference was even greater, 0.4 log E, when comparing the two emulsions at more nearly equal maximum densities. At the direct viewing conditions (1:1 magnification) normally used for products of this type, there was no difference in graininess apparent upon visual inspection.

Emulsion	Pod	D _G -max	D _G -min	Green Contrast	Relative Green Speed
Control-A-2	L	1.3	0.13	1.4	100
Tabular Grain Emulsion C	L	1.8	0.13	2.0	119
Control-A-2	M	1.6	0.13	1.6	77
Tabular Grain Emulsion C	M	1.9	0.13	1.8	99

Example 3

A multicolor integral imaging receiver (IIR) of the following structure was prepared:

- Overcoat layer
- Yellow imaging layer
- Interlayer
- Magenta imaging layer: Green-sensitized negative silver bromoiodide Tabular Grain Emulsion D (a remake of Tabular Grain Emulsion C) (0.65 Ag), Redox Dye Releaser (0.63), Reducing Agent (0.32), PMT Inhibitor (0.010), TAI Antifoggant (3.6 g/Ag mole), gelatin (1.3)
- Interlayer
- Cyan imaging layer
- Gelatin interlayer
- Opaque layer
- Reflecting layer
- Mordant layer: Poly(4-vinylpyridine) (2.2), gelatin (2.2)
- Metal-containing layer: Nickel sulfate hexahydrate (0.58), gelatin (1.1)

The layers were coated on clear polyester support in the order of numbering.

A control was similar to the example, but used a low-aspect ratio silver bromoiodide emulsion, A-3, at 0.99 g Ag/m² in layer 8, the magenta imaging layer.

Both the example and the control were hardened. The cover sheet was the same as was used for Example 2. Processing pods of the following composition were prepared:

	Pod N
Potassium hydroxide	60.0 g/l
4-Hydroxymethyl-4-methyl-1-p-tolyl-3-pyrazolidinone	12.0 g/l
Potassium bromide	5.0 g/l
Ethylenediaminetetraacetic acid, disodium salt	10.0 g/l
Carboxymethylcellulose	57.0 g/l

The above elements were used as follows:

The multicolor integral imaging receiver (IIR) was exposed in a sensitometer to give a neutral image at a Status A density of 1.0 after processing with a viscous processing composition in a pod. The pod contents were spread between the IIR and the cover sheet using a pair of rollers which provide a 100 μm gap. Within 12 to 24 hours the Status A green density of the receiver side of the IIR was read to obtain the sensitometric curve. The green density sensitometric parameters, D_{max}, D_{min}, contrast, and relative speed (at D = 0.2 below D_{max}) were read from the curve.

The data below shows that the Tabular Grain Emulsion D, had a relative speed that was almost 0.3 log E faster than the control, yet used only 2/3 the quantity of silver. Again, at the direct viewing conditions (1:1 magnification) used for products of this type, no significant difference in 'observed graininess' was seen as viewed through a green filter.

Emulsion	Pod	D _G -max	D _G -min	Green Contrast	Relative Green Speed
Control A-3	N	1.9	0.12	1.5	100
Tabular Emulsion D	N	2.0	0.23	1.4	127

Example 4

Tabular Grain Emulsion E

A high aspect ratio tabular grain silver chloride emulsion having an average grain diameter of 6.0 micron, an average grain thickness of 0.28 microns and an average aspect ratio of 22:1 was prepared. The tabular silver chloride grains accounted for greater than 80 percent of the total projected area. The emulsion was optimally sensitized chemically with sulfur and gold in the presence of thiocyanate and spectrally sensitized to green light with an oxacarbocyanine dye in the presence of 3 mole percent bromide.

Dye Image Transfer Film Units

Integral imaging receivers (IIR's using Tabular Emulsion C were otherwise identical to those of Example 2.

The cover sheet and the pods L and N are the same as those of Examples 2 and 3.

The above elements were used in the manner described in Example 2.

The above IIR using Emulsion E yielded a full-scale D_{min}/D_{max} image when exposed in an Eastman IB Sensitometer at 1/100 sec through a graduated density test object. This indicates that Emulsion E had sufficient photographic sensitivity to be considered suitable for 'camera-speed' use with image transfer materials. Sensitometric parameters are tabulated below.

Emulsion	Pod	D _G -max	D _G -min	Green Contrast
E	L	1.6	≈0.3	1.1
E	N	1.0	0.31	0.7

Example 5

Tabular Grain Emulsion F

A high aspect ratio tabular silver bromoiodide host emulsion sensitized with silver chloride epitaxial deposition with an average grain diameter of 3.0 microns, an average grain thickness of 0.09 micron and an average aspect ratio of 33:1 was prepared. The tabular grains accounted for greater than 85 percent of the total grain surface area.

An integral imaging receiver (IIR) was prepared similar to that of Example 2, except: in layer 6, Tabular Emulsion F was used (0.67 Ag), and layer 5 was omitted.

The cover sheet and pod N were the same as Examples 2 and 3. The above elements were used in the same manner as described in the referenced Example 2.

The above IIR using Emulsion F yielded a full-scale D_{min}/D_{max} image when exposed in an Eastman IB Sensitometer at 1/100 sec through a graduated density test object. This indicates that Emulsion F had sufficient photographic sensitivity to be considered suitable for 'camera-speed' use with image transfer materials. Sensitometric parameters are tabulated below.

Emulsion	Pod	D _G -max	D _G -min	Green Contrast
F	N	2.0	≈0.15	2.1

The most commonly employed photographic elements are those containing one or more radiation-sensitive silver halide emulsion layers. Their widespread use is attributable to the

excellent quality images they are capable of producing and to their high speed, allowing them to be employed in hand-held cameras under a variety of lighting conditions.

Nevertheless, silver halide photographic elements have historically exhibited two significant limitations in terms of viewing the photographic image. First, imagewise exposure of the silver halide emulsion layer does not produce an immediately viewable photographic image. Exposure produces an invisible latent image in the silver halide emulsion. Processing of the latent image is required to produce a viewable image. Historically this has meant removing the photographic element from the camera and processing in one or more aqueous solutions to obtain a viewable image. Second, in most instances the first viewable image obtained is a negative image, and a second exposure through the negative image of an additional photographic element and processing thereof is required to produce a viewable positive of the image initially photographed. The first limitation can be overcome by employing image transfer techniques, and the second limitation can be overcome by employing direct-positive imaging, particularly direct reversal imaging.

Photographic elements which produce images having an optical density directly related to the radiation received on exposure are said to be negative-working. A positive photographic image can be formed by producing a negative photographic image and then forming a second photographic image which is a negative of the first negative — that is, a positive image. A direct-positive image is understood in photography to be a positive image that is formed without first forming a negative image. Positive dye images which are not direct-positive images are commonly produced in color photography by reversal processing in which a negative silver image is formed and a complementary positive dye image is then formed in the same photographic element. The term 'direct reversal' has been applied to direct-positive photographic elements and processing which produces a positive dye image without forming a negative silver image. Direct-positive photography in general and direct reversal photography in particular are advantageous in providing a more straight-forward approach to obtaining positive photographic images.

A conventional approach to forming direct-positive images is to use photographic elements employing internal latent image-forming silver halide grains. After imagewise exposure, the silver halide grains are developed with a surface developer — that is, one which will leave the latent image sites within the silver halide grains substantially unrevealed. Simultaneously, either by uniform light exposure or by the use of a nucleating agent, the silver halide grains are subjected to development conditions that would cause fogging of a surface latent image-forming photographic element. The internal latent image-forming silver halide grains which received actinic radiation during imagewise exposure develop under these conditions at a slow rate as compared to the internal latent image-forming silver halide grains not imagewise exposed. The result is a direct-positive silver image. In color photography, the oxidized developer that is produced during silver development is used to produce a corresponding positive, direct reversal dye image. Multi-color direct reversal photographic images have been extensively investigated in connection with image transfer photography.

It has been found advantageous to employ nucleating agents in preference to uniform light exposure in the process described above. The term 'nucleating agent' is employed herein in its art-recognized usage to mean a fogging agent capable of permitting the selective development of internal latent image-forming silver halide grains which have not been imagewise exposed in preference to the development of silver halide grains having an internal latent image formed by image-wise exposure.

While nucleating agents have been long known to the photographic art, recent interest has focused on identifying nucleating agents that are effective in relatively low concentration levels and that can be incorporated directly into silver halide emulsions. Exemplary of known incorporated nucleating agents are those disclosed by Whitmore US Patent 3,227,552, Lincoln et al US Patent 3,615,615, Kurtz et al US Patents 3,719,494 and 3,734,738, Lincoln et al US Patent 3,759,901, Leone et al US Patents 4,030,925, 4,080,207, and 4,276,364, Adachi et al US Patent 4,115,122, von Konig et al US Patent 4,139,387, and UK Patents 2,011,391 and 2,012,443. Nucleating agents particularly adapted for use in direct reversal photographic elements intended to be processed at lower pH levels are disclosed by Baralle et al US Patents 4,306,016, 4,306,017, and 4,315,986.

Direct reversal emulsions exhibit art-recognized disadvantages as compared to negative-working emulsions. Although Evans, cited above, has been able to increase photographic speeds by properly balancing internal and surface sensitivities, direct reversal emulsions have not achieved photographic speeds equal to the faster surface latent image-forming emulsions. Second, direct reversal emulsions are limited in their permissible exposure latitude. When exposure is extended reversal occurs. That is, in areas receiving extended exposure a negative image is produced. This is a significant limitation to in-camera use of direct reversal photographic elements, since candid photography does not always permit control of exposure conditions. For example, a very high contrast scene can lead to rereversal in some image areas.

In one aspect this disclosure describes a radiation-sensitive emulsion particularly adapted to forming a direct-positive image comprised of a dispersing medium, silver halide grains capable of forming an internal latent image, and a nucleating agent. At least 50 percent of the total projected area of the silver halide grains is provided by tabular grains which have an average thickness of less than 0.5 micron, preferably an average diameter of at least 0.6 micron, and an average aspect ratio of greater than 8:1. This disclosure also describes a photographic element comprised of a support and at least one radiation-sensitive emulsion layer comprised of a radiation-sensitive emulsion as described above. In an additional aspect, this disclosure describes to a photographic image transfer film unit comprising at least one emulsion as described above.

In addition to the advantages common to the negative-working tabular grain emulsions of this disclosure described above, direct-positive and, more specifically, direct reversal images can be produced while realizing also improved stability and less image dependence on temperature as compared to nontabular direct reversal emulsions. Further, the emulsions of the present disclosure in certain preferred embodiments permit wider exposure latitude without encountering rereversal.

The emulsions employed to form direct positive and direct reversal images are the high aspect ratio tabular grain internal latent image-forming emulsions previously described. The emulsions are also comprised of a dispersing medium, silver halide grains capable of forming an internal latent image, and a nucleating agent.

The high aspect ratio tabular grain internal latent image-forming emulsions of this disclosure can be prepared merely by modifying the processes for preparing high aspect ratio tabular grain emulsions described above to favor the formation of internal latent image centers on exposure. This can be accomplished by employing techniques similar to those demonstrated in the examples of Porter et al US Patent 3,206,313, Evans US Patents 3,761,276 and 3,923,513, and Atwell et al US Patent 4,035,185, cited above to illustrate conventional direct reversal emulsions and here incorporated by reference. Typically internal latent image-forming silver halide grains prepared by such techniques have an average diameter of at least 0.6 micron, and the preferred tabular grains of this disclosure also exhibit an average diameter of at least 0.6 micron. Since the tabular quality of high aspect ratio grains is degraded by high levels of halide conversion, the use of halide conversion techniques is not preferred in the practice of this disclosure. Specific preferred techniques for modifying high aspect ratio tabular grain emulsions during their preparation to favor the formation of internal latent image centers are described below.

Perhaps the simplest manipulative approach to favoring internal latent image formation is to incorporate a metal dopant within the tabular grains as they are being formed. The metal dopant can be placed in the reaction vessel in which grain formation occurs prior to the introduction of silver salt. Alternately the metal dopant can be introduced during silver halide grain growth at any stage of precipitation, with or without interrupting silver and/or halide salt introduction.

Iridium is specifically contemplated as a metal dopant. It is preferably incorporated within the silver halide grains in concentrations of from about 10^{-8} to 10^{-4} mole per mole of silver. The iridium can be conveniently incorporated into the reaction vessel as a water soluble salt, such as an alkali metal salt of a halogen-iridium coordination complex, such as sodium or potassium hexachloroiridate or hexabromoiridate. Specific examples of incorporating an iridium dopant are provided by Berriman US Patent 3,367,778.

Lead is also a specifically contemplated metal dopant for promoting the formation of internal latent image centers. Lead is a common dopant in direct print and printout emulsions and can be employed in the practice of this disclosure in similar concentration ranges. It is generally preferred that the lead dopant be present in a concentration of at least 10^{-4} mole per mole of silver. Concentrations up to about 5×10^{-2} , preferably 2×10^{-2} , mole per mole of silver are contemplated. Lead dopants can be introduced similarly as iridium dopants in the form of water soluble salts, such as lead acetate, lead nitrate, and lead cyanide. Lead dopants are particularly illustrated by McBride US Patent 3,287,136 and Bacon US Patent 3,531,291.

Another technique for promoting the formation of internal latent image centers is to stop silver halide grain precipitation after a grain nucleus or core has been produced and to sensitize chemically the surface of the core. Thereafter additional precipitation of silver halide produces a shell surrounding the core. Particularly advantageous chemical sensitizers for this purpose are middle chalcogen sensitizers — ie, sulfur, selenium, and/or tellurium sensitizers. Middle chalcogen sensitizers are preferably employed in concentrations in the range of from about 0.05 to 15 mg per silver mole. Preferred concentrations are from about 0.1 to 10 mg per silver mole. Further advantages can be realized by employing a gold sensitizer in combination. Gold sensitizers are preferably employed in concentrations ranging from 0.5 to 5 times that of the middle chalcogen sensitizers. Preferred concentrations of gold sensitizers typically range from about 0.01 to 40 mg per mole of silver, most preferably from about 0.1 to 20 mg per mole of silver. Controlling contrast by controlling the ratio of middle chalcogen

to gold sensitizer is particularly taught by Atwell et al US Patent 4,035,185, cited above and here incorporated by reference specifically for this teaching. Evans, cited above, provides specific examples of middle chalcogen internal sensitizations.

Although it is usually preferred to produce internal sensitization sites by the occlusion of foreign (ie, other than silver and halogen) materials within the tabular grains, this is not required. Sensitization sites formed by the occlusion of foreign materials are hereinafter referred to as internal chemical sensitization sites to distinguish them from internal physical sensitization sites. It is possible to incorporate internal physical sensitization sites by providing irregularities in the crystal lattice for capturing photolytically generated electrons. Such internal irregularities can be created by discontinuities in silver halide grain precipitation or by abrupt changes in the halide content of the tabular grains. For example, it has been observed that the precipitation of a tabular silver bromide core followed by shelling with silver bromoiodide of greater than 5 mole percent iodide requires no internal chemical sensitization to produce a direct reversal image.

Silver halide surrounds the internal sensitization sites within the tabular grains. The minimum amount of overlying silver halide is just that required to prevent access of the developer employed in processing to the internal latent image. This will vary as a function of the ability of the developer to dissolve the silver halide grains during development. For developers having very low silver halide solvency the latent image centers can be located only a few crystal lattice planes below the surface of the tabular silver halide grains. If the internal latent image center forms at or near the center of the grain, as where a metal dopant is present in the reaction vessel at the start of silver halide precipitation, then all or most of the silver halide forming the grain will lie between the latent image center and the grain surface. On the other hand, if a tabular silver halide grain is precipitated to substantially its final size and aspect ratio before internal sensitization, the addition of only a small amount of additional silver halide is needed to protect the sensitization sites from a surface or sub-surface developer. The placement of internal sensitization sites in silver halide grains is particularly illustrated by Morgan US Patent 3,917,485 and *Research Disclosure*, Vol 181, May 1979, Item 18155. Since grain nuclei formation is critical to obtaining tabular grains of high aspect ratio, it is generally preferred to delay internal sensitization until at least the commencement of the growth stage of tabular grain formation. When internal sensitization is delayed until the tabular grains have substantially achieved their desired size and aspect ratio, then additional silver halide can be precipitated onto the tabular grains by any conventional silver halide precipitation technique, including Ostwald ripening of a blended shell emulsion as taught by Porter et al US Patents 3,206,313 and 3,317,322.

The amount of overexposure which can be tolerated without encountering rereversal can be increased by incorporating into the tabular silver halide grains metal dopants for this purpose. The use of divalent and trivalent metal ions as dopants in the core or shell of core-shell emulsions to reduce rereversal is specifically contemplated. Preferred metal dopants for this purpose are cationic cadmium, zinc, lead, lanthanides (particularly erbium), manganese, copper, and bismuth. These dopants are generally effective at concentration levels of 10^{-3} - 10^{-7} mole/Ag mole. The rereversal modifying dopant is effective if introduced at any stage of silver halide precipitation. If the tabular silver halide grains are viewed as being comprised of a core and a shell, the rereversal modifying dopant can be incorporated in either or both of the core and shell. The metal dopants can be introduced into the reaction vessel as water soluble metal salts, such as divalent and trivalent metal halide salts. Dopants for silver halide in similar concentrations, but to achieve other modifying effects, are disclosed by McBride US Patent 3,287,136, Mueller et al US Patent 2,950,972, Iwaosa et al US Patent 3,901,711, and Atwell US Patent 4,269,927. Other techniques for improving rereversal characteristics discussed below can be employed independently or in combination with the metal dopants described.

The high aspect ratio tabular grain internal latent image-forming emulsions of the present disclosure are preferably intentionally surface chemically sensitized to increase their photographic speed. Useful surface chemical sensitizations are taught by Evans US Patent 3,761,276 and 3,923,513 and Atwell et al US Patent 4,035,185, each previously cited and here incorporated by reference for their specific teaching. Any type of surface chemical sensitization known to be useful with corresponding surface latent image-forming silver halide emulsions can be employed, but the degree of surface chemical sensitization is limited to that which will increase the reversal speed of the internal latent image-forming emulsion, but which will not compete with the internal sensitization sites to the extent of causing the location of latent image centers formed on exposure to shift from the interior to the surface of the tabular grains.

Thus, a balance between internal and surface sensitization is preferably maintained for maximum speed, but with the internal sensitization predominant. Tolerable levels of surface chemical sensitization can be readily determined by the following test: A

sample of the high aspect ratio tabular grain internal latent image-forming silver halide emulsion of the present disclosure is coated on a transparent film support at a silver coverage of 4 grams per square meter. The coated sample is then exposed to a 500 watt tungsten lamp for times ranging from 0.01 to 1 second at a distance of 0.6 meter. The exposed coated sample is then developed for 5 minutes at 20°C in Developer Y below (an 'internal type' developer, note the incorporation of iodide to provide access to the interior of the grain), fixed, washed, and dried. The procedure described above is repeated with a second sample identically coated and exposed. Processing is also identical, except that Developer X below (a 'surface type' developer) is substituted for Developer Y. To satisfy the requirements of the present disclosure as being a useful internal latent image-forming emulsion the sample developed in the internal type developer, Developer Y, must exhibit a maximum density at least 5 times greater than the sample developed in the surface type developer, Developer X. This difference in density is a positive indication that the latent image centers of the silver halide grains are forming predominantly in the interior of the grains and are for the most part inaccessible to the surface type developer.

Developer X	Grams
N-methyl-p-aminophenol sulfate	2.5
Ascorbic acid	10.0
Potassium metaborate	35.0
Potassium bromide	1.0
Water to 1 liter.	
Developer Y	Grams
N-methyl-p-aminophenol sulfate	2.0
Sodium sulfite, desiccated	90.0
Hydroquinone	8.0
Sodium carbonate, monohydrate	52.5
Potassium bromide	5.0
Potassium iodide	0.5
Water to 1 liter.	

The high aspect ratio tabular grain internal latent image-forming silver halide emulsions of the present disclosure can be surface chemically sensitized and spectrally sensitized by the same techniques described above in relation to negative-working emulsions.

The high aspect ratio tabular grain internal latent image-forming emulsions of this disclosure incorporate a nucleating agent to promote the formation of a direct-positive image upon processing. The nucleating agent can be incorporated in the emulsion during processing, but is preferably incorporated in manufacture of the photographic element, usually prior to coating. This reduces the quantities of nucleating agent required. The quantities of nucleating agent required can also be reduced by restricting the mobility of the nucleating agent in the photographic element. Large organic substituents capable of performing at least to some extent a ballast function are commonly employed. Nucleating agents which include one or more groups to promote adsorption to the surface of the silver halide grains have been found to be effective in extremely low concentrations.

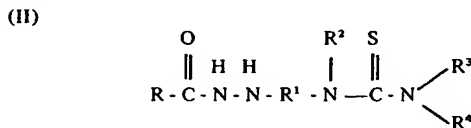
A preferred general class of nucleating agents for use in the practice of this disclosure are aromatic hydrazides. Particularly preferred aromatic hydrazides are those in which the aromatic nucleus is substituted with one or more groups to restrict mobility and, preferably, promote adsorption of the hydrazide to silver halide grain surfaces. More specifically, preferred hydrazides are those embraced by formula (I) below:



wherein

D is an acyl group;
 \bigcirc is a phenylene or substituted (eg, halo-, alkyl-, or alkoxy-substituted) phenylene group; and
M is a moiety capable of restricting mobility, such as an adsorption promoting moiety.

A particularly preferred class of phenylhydrazides are acylhydrazinophenylthiureas represented by formula (II) below.



wherein

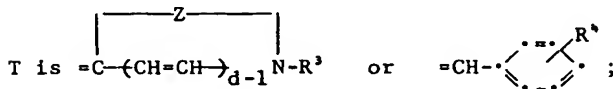
R is hydrogen or an alkyl, cycloalkyl, haloalkyl, alkoxy-alkyl, or phenylalkyl substituent or a phenyl nucleus having a

X is $=S$ or $=O$.

Another specifically preferred subclass of heterocyclic thioamide nuclei is formed when Q' is as indicated in formula (V)

$$\begin{array}{c} \text{X} \\ \parallel \quad | \\ \cdot \text{C} - \text{C} = \text{C} \text{L} - \text{L} = \text{C}_{n-1} \text{T} \end{array}$$

L is a methine group;



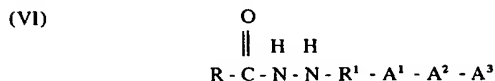
R' is hydrogen; an alkyl, $-N \begin{smallmatrix} R^5 \\ R^6 \end{smallmatrix}$, or an

Z represents the nonmetallic atoms necessary to complete a basic heterocyclic nucleus of the type found in cyanine dyes; n and d are independently chosen from the integers 1 and 2; R⁵ and R⁶ are independently chosen from hydrogen, phenyl, alkyl, alkylphenyl, and phenylalkyl; and the alkyl moieties in each instance include from 1 to 6 carbon atoms.

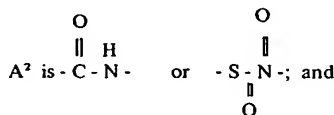
The formula (V) values for Q^1 provide a heterocyclic thioamide nucleus corresponding to a methine substituted form of the nuclei present above in formula (IV) values for Q^1 . In a specifically preferred form the heterocyclic thioamide nucleus is preferably a methine substituted 2-thiohydantoin, rhodanine, isorhodanine, or 2-thio-2,4-oxazolidinedione nucleus. The heterocyclic thioamide nucleus of formula (V) is directly, or through an intermediate methine linkage, substituted with a basic heterocyclic nucleus of the type employed in cyanine dyes or a substituted benzylidene nucleus. Z preferably represents the nonmetallic atoms necessary to complete a basic 5- or 6-membered heterocyclic nucleus of the type found in cyanine dyes having ring-forming atoms chosen from the class consisting of carbon, nitrogen, oxygen, sulfur, and selenium.

N-(acylhydrazinophenyl)thioamide nucleating agents and their synthesis are more specifically disclosed in Leone et al US Patent 4,080,207.

Still another preferred class of phenylhydrazide nucleating agents are triazole-substituted phenylhydrazide nucleating agents. More specifically, preferred triazole-substituted phenylhydrazide nucleating agents are those represented by formula VI below:

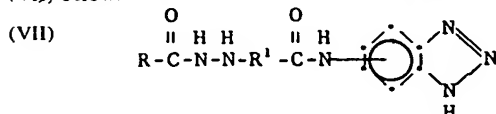


R and R' are as defined in formula (II);
A' is alkylene or oxalkylene;

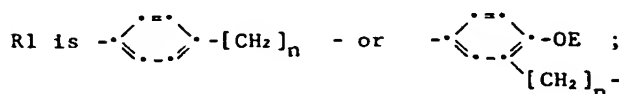


A³ is a triazolyl or benzotriazolyl nucleus;
the alkyl and alkylene moieties in each instance including
from 1 to 6 carbon atoms.

Still more specifically preferred triazole-substituted phenylhydrazide nucleating agents are those represented by formula (VII) below:



R is hydrogen or methyl;

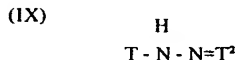
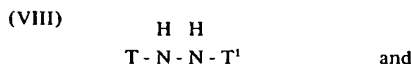


E is alkyl of from 1 to 4 carbon atoms.

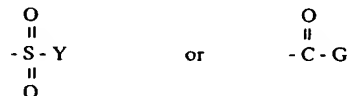
Triazole-substituted phenylhydrazide nucleating agents and their synthesis are disclosed by Sidhu et al US Patent 4,278,748, here incorporated by reference. Comparable nucleating agents having a somewhat broader range of adsorption promoting groups are disclosed in corresponding UK Patent Application 2,011,391A.

The aromatic hydrazides represented by formulas (II), (III), and (VI) each contain adsorption promoting substituents. In many instances it is preferred to employ in combination with these aromatic hydrazides additional hydrazides or hydrazones which do not contain substituents specifically intended to promote adsorption to silver halide grain surfaces. Such hydrazides or hydrazones, however, often contain substituents to reduce their mobility when incorporated in photographic elements. These hydrazide or hydrazones can be employed as the sole nucleating agent, if desired.

Such hydrazides and hydrazones include those represented by formula (VIII) and (IX) below:



wherein T is an aryl radical, including a substituted aryl radical, T¹ is an acyl radical, and T² is an alkylidene radical and including substituted alkylidene radicals. Typical aryl radicals for the substituent T have the formula M-T³·, wherein T³ is an aryl radical (such as, phenyl, 1-naphthyl, 2-naphthyl, etc) and M can be such substituents as hydrogen, hydroxy, amino, alkyl, alkylamino, aryl-amino, heterocyclic amino (amino containing a heterocyclic moiety), alkoxy, aryloxy, acyloxy, arylcarbonamido, alkylcarbon-amido, heterocyclic carbonamido (carbonamido containing a heterocyclic moiety), arylsulfonamido, alkylsulfonamido, and heterocyclic sulfonamido (sulfonamido containing a heterocyclic moiety). Typical acyl radicals for the substituent T¹ have the formula



wherein Y can be such substituents as alkyl, aryl, and heterocyclic radicals, G can represent a hydrogen atom or the same substituent as Y as well as radicals having the formula

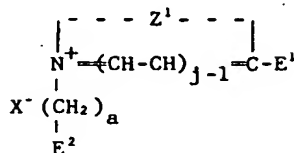


to form oxalyl radicals wherein A is an alkyl, aryl, or a heterocyclic radical. Typical alkylidene radicals for the substituent T² have the formula =CH-D wherein D can be a hydrogen atom or such radicals as alkyl, aryl, and heterocyclic radicals. Typical aryl substituents for the above-described hydrazides and hydrazones include phenyl, naphthyl, diphenyl, and the like. Typical heterocyclic substituents for the above-described hydrazides and hydrazones include azoles, azines, furan, thiophene, quinoline, pyrazole, and the like. Typical alkyl (or alkylidene) substituents for the above-described hydrazides and hydrazones have 1 to 22 carbon atoms including methyl, ethyl, isopropyl, *n*-propyl, isobutyl, *n*-butyl, *t*-butyl, amyl, *n*-octyl, *n*-decyl, *n*-dodecyl, *n*-octadecyl, *n*-eicosyl, and *n*-docosyl.

The hydrazides and hydrazones represented by formulas (VIII) and (IX) as well as their synthesis are disclosed by Whitmore US Patent 3,227,552, here incorporated by reference.

A secondary preferred general class of nucleating agents for use in the practice of this disclosure are N-substituted cycloammonium quaternary salts. A particularly preferred species of such nucleating agents is represented by formula (X) below:

(X)



wherein

Z¹ represents the atoms necessary to complete a heterocyclic nucleus containing a heterocyclic ring of 5 to 6 atoms including the quaternary nitrogen atoms, with the additional atoms of said heterocyclic ring being selected from carbon, nitrogen, oxygen, sulfur, and selenium;

j represents a positive integer of from 1 to 2;

a represents a positive integer of from 2 to 6;

X^- represents an acid anion;

E² represents a member selected from (a) a formyl radical, (b) a radical having the formula



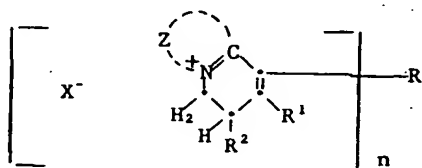
wherein each of L¹ and L², when taken alone, represents a member selected from an alkoxy radical and an alkylthio radical, and L¹ and L², when taken together, represent the atoms necessary to complete a cyclic radical selected from cyclic oxyacetals and cyclic thioacetals having from 5 to 6 atoms in the heterocyclic acetal ring, and (c) a 1-hydrazonoalkyl radical; and

E¹ represents either a hydrogen atom, an alkyl radical, an aralkyl radical, an alkylthio radical, or an aryl radical such as phenyl and naphthyl, and including substituted aryl radicals.

The N-substituted cycloammonium quaternary salt nucleating agents of formula (X) and their synthesis are disclosed by Lincoln and Heseltine US Patents 3,615,615 and 3,759,901. In a variant form E¹ can be a divalent alkylene group of from 2 to 4 carbon atoms joining two substituted heterocyclic nuclei as shown in formula (X). Such nucleating agents and their synthesis are disclosed by Kurtz and Harbison US Patent 3,734,738.

The substituent to the quaternized nitrogen atom of the heterocyclic ring can, in another variant form, itself form a fused ring with the heterocyclic ring. Such nucleating agents are illustrated by dihydroaromatic quaternary salts comprising a 1,2-dihydroaromatic heterocyclic nucleus including a quaternary nitrogen atom. Particularly advantageous 1,2-dihydroaromatic nuclei include such nuclei as a 1,2-dihydropyridinium nucleus. Especially preferred dihydroaromatic quaternary salt nucleating agents include those represented by formula (XI) below:

(XI)



wherein

Z represents the nonmetallic atoms necessary to complete a heterocyclic nucleus containing a heterocyclic ring of from 5 to 6 atoms including the quaternary nitrogen atom, with the additional atoms of said heterocyclic ring being selected from either carbon, nitrogen, oxygen, sulfur, or selenium;

2: n represents a positive integer having a value of from 1 to

when n is 1, R represents a member selected from the group consisting of a hydrogen atom, an alkyl radical, an alkoxy radical, an aryl radical, an aryloxy radical, and a carbamido radical and,

when n is 2, R represents an alkylene radical having from 1 to 4 carbon atoms:

each of R¹ and R² represents a member selected from the group consisting of a hydrogen atom, an alkyl radical, and an aryl radical; and

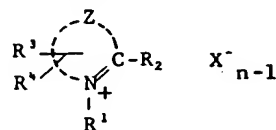
X represents an anion.

Dihydroaromatic quaternary salt nucleating agents and their syntheses are disclosed by Kurtz and Heseltine US Patents 3,719,494, here incorporated by reference.

A specifically preferred class of N-substituted cycloammonium quaternary salt nucleating agents are those which include one or more alkynyl substituents. Such nucleating agents include com-

pounds within the generic structural definition set forth in formula (XII) below:

(XII)



wherein Z represents an atomic group necessary for forming a 5- or 6-membered heterocyclic nucleus, R¹ represents an aliphatic group, R² represents a hydrogen atom or an aliphatic group, R³ and R⁴, which may be the same or different, each represents a hydrogen atom, a halogen atom, an aliphatic group, an alkoxy group, a hydroxy group, or an aromatic group, at least one of R¹, R², R³ and R⁴ being a propargyl group, a butynyl group, or a substituent containing a propargyl or butynyl group, X⁻ represents an anion, n is 1 or 2, with n being 1 when the compound forms an inner salt.

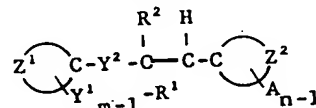
Such alkynyl-substituted cycloammonium quaternary salt nucleating agents and their synthesis are illustrated by Adachi et al US Patent 4,115,122, here incorporated by reference.

The specific choice of nucleating agents can be influenced by a variety of factors. The nucleating agents of Leone cited above are particularly preferred for many applications, since they are effective at very low concentrations. Minimum concentrations as low as 0.1 mg of nucleating agent per mole of silver, preferably at least 0.5 mg per silver mole, and optimally at least 1 mg per silver mole are disclosed by Leone. The nucleating agents of Leone are particularly advantageous in reducing speed loss and in some instances permitting speed gain with increasing processing temperatures. When the nucleating agents of Leone are employed in combination with those of Whitmore speed variations as a function of temperature of processing can be minimized.

The aromatic hydrazide nucleating agents are generally preferred for use in photographic elements intended to be processed at comparatively high levels of pH, typically above 13. The alkynyl-substituted cycloammonium quaternary salt nucleating agents are particularly useful for processing at a pH of 13 or less. Adachi et al teaches these nucleating agents to be useful in processing within the pH range of from 10 to 13, preferably 1.1 to 12.5.

In addition to the nucleating agents described above additional nucleating agents have been identified which are useful in processing at pH levels in the range of from about 10 to 13. An N-substituted cycloammonium quaternary salt nucleating agent which can contain one or more alkynyl substituents is illustrative of one class of nucleating agents useful in processing below pH 13. Such nucleating agents are illustrated by formula (XIII) below:

(XIII)



wherein

Z¹ represents the atoms completing an aromatic carbocyclic nucleus of from 6 to 10 carbon atoms;

Y¹ and Y² are independently selected from among a divalent oxygen atom, a divalent sulfur atom and

$$\begin{array}{c} | \\ -\text{N}-\text{R}^3: \end{array}$$

Z^2 represents the atoms completing a heterocyclic nucleus of the type found in cyanine dyes;

A is an adsorption promoting moiety;

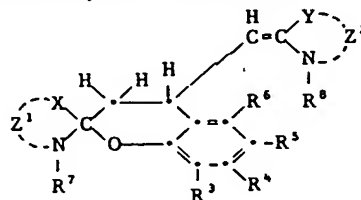
m and n are 1 or 2; and

R^1 , R^2 , and R^3 are independently chosen from the group consisting of hydrogen, alkyl, aryl, alkaryl, and aralkyl and R^1 and R^2 are additionally independently chosen from the group consisting of acyl, alkenyl, and alkynyl, the aliphatic moieties containing up to 5 carbon atoms and the aromatic moieties containing 6 to 10 carbon atoms. A preferred processing pH when these nucleating agents are employed is in the range of from 10.2 to 12.0.

Nucleating agents of the type represented by formula (XIII) and their synthesis are disclosed by Baralle et al US Patent 4,306,016, cited above, and here incorporated by reference.

Another class of nucleating agents effective in the pH range of from 10 to 13, preferably 10.2 to 12, are dihydrospiropyran bis-condensation products of salicylic aldehyde and at least one heterocyclic ammonium salt. In a preferred form such nucleating agents are represented by formula (XIV) below:

(XIV)



wherein

X and Y each independently represent a sulfur atom, a selenium atom or a $-C(R^1 R^2)-$ radical,

R^1 and R^2 independently represent lower alkyl of from 1 to 5 carbon atoms or together represent an alkylene radical of 4 or 5 carbon atoms,

R^3 , R^4 , R^5 , and R^6 each represent hydrogen, a hydroxy radical or a lower alkyl or alkoxy radical of from 1 to 5 carbon atoms,

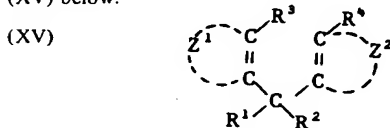
Z^1 and Z^2 each represents the nonmetallic atoms completing a nitrogen-containing heterocyclic nucleus of the type found in cyanine dyes and

R^7 and R^8 each represent a ring nitrogen substituent of the type found in cyanine dyes.

Z^1 and Z^2 in a preferred form each completes a 5- or 6-membered ring, preferably fused with at least one benzene ring, containing in the ring structure carbon atoms, a single nitrogen atom and, optionally, a sulfur or selenium atom.

Nucleating agents of the type represented by formula (XIV) and their synthesis are disclosed by Baralle et al US Patent 4,306,017, cited above, and here incorporated by reference.

Still another class of nucleating agents effective in the pH range of from 10 to 13, preferably 10.2 to 12, are diphenylmethane nucleating agents. Such nucleating agents are illustrated by formula (XV) below:

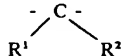


wherein

Z^1 and Z^2 represent the atoms completing a phenyl nucleus;

R^1 represents hydrogen or alkyl of from 1 to 6 carbon atoms; and

R^2 , R^3 , and R^4 are independently selected from among hydrogen, halogen, alkyl, hydroxy, alkoxy, aryl, alkaryl, and aralkyl or R^3 and R^4 together form a covalent bond, a divalent chalcogen linkage, or



wherein each alkyl moiety contains from 1 to 6 carbon atoms and each aryl moiety contains 6 to 10 carbon atoms.

Nucleating agents of the type represented by formula (XV) and their synthesis are disclosed by Baralle et al US Patent 4,315,986, cited above, and here incorporated by reference.

Once high aspect ratio tabular grain internal latent image-forming emulsions have been generated by precipitation procedures, washed, and sensitized, as described above, their preparation can be completed by the incorporation of nucleating agents, described above, and conventional photographic addenda, and they can be usefully applied to photographic applications requiring a dye or silver image to be produced — eg, conventional, color or black-and-white photography. For image transfer applications Layer Order Arrangements generally similar to those described above for negative-working high aspect ratio tabular grain emulsions can be employed. It is specifically contemplated to substitute the internal latent-image-forming silver halide grains of this disclosure for the silver halide grains present in a PR-10 image transfer film unit.

The disclosure can be better appreciated by reference to the following illustrative examples.

Emulsion A Core Tabular AgBr Emulsion

The tabular AgBr grains of the core emulsion had a mean grain diameter of 1.0 μ m, an average thickness of 0.08 μ m, and an average aspect ratio of 12.5:1 and accounted for greater than 90 percent of the total projected area of the silver halide grains. Emulsion A was sulfur and gold sensitized.

Emulsion B Core/Shell Tabular AgBr Emulsion

The chemically sensitized Emulsion A (0.22 mole) was shelled with silver bromide. The resulting AgBr crystals had a mean grain diameter of 3.0 μ m, an average thickness of 0.25 μ m, and average aspect ratio of 12:1.

Emulsion B was chemically sensitized with sulfur and gold.

Emulsion C Cadmium Doped Tabular AgBr Internal Latent Image-Forming Emulsion

Emulsion C was prepared the same as Emulsion B with the exception that into the shelling stage of the core/shell precipitation cadmium bromide was added at 0.05 mole percent (based on the moles of silver in the shell).

Emulsion D Control Emulsion

A 1.8 μ m monodispersed internal image octahedral AgBr emulsion similar to that described in Example 7 of Evans US Patent 3,923,513, was used as a control for the above emulsion. The 1.25 μ m core emulsion was sulfur and gold sensitized.

Example 1A

This example shows that a red-sensitized tabular grain internal latent image-forming emulsion, Emulsion B, provides an advantage in developability over an extended temperature range compared to a red-sensitized internal latent image-forming octahedral grain emulsion, Emulsion D, as used in a multicolor image transfer latent element using sulfonamidonaphthol redox dye-release (RDR) chemistry.

An integral imaging receiver (IIR) of the following layer order arrangement was prepared: Coverages are in (g/m²) or (mg/Ag mole). Redox dye-releasers (RDR's) are of the structures described in *Research Disclosure*, Vol 182, July 1979, Item 1828, pages 329-31.

Layer 16: Overcoat Layer: Scavenger (0.11), gelatin (0.89), Hardener at 1 percent of the total gelatin weight

Layer 15: Blue-sensitive silver halide layer: The emulsion is similar to the octahedral grain control Emulsion D, except that it is blue-sensitized. Silver halide (1.34 Ag), Formula (I) nucleating agent [13.0], Formula (II) nucleating agent [0.41], scavenger [4000], gelatin (1.34).

Layer 14: Interlayer: Titanium dioxide (0.27), gelatin (0.65)

Layer 13: Yellow dye-releaser layer: Yellow RDR (0.65), gelatin (0.86)

Layer 12: Interlayer: Negative silver bromide emulsion (0.11 Ag), scavenger (1.1), gelatin (1.3)

Layer 11: Green-sensitive silver halide layer: The emulsion is similar to the octahedral grain control Emulsion D, except that it is green-sensitized. Silver halide (1.34 Ag), Formula (I) nucleating agent [17.0], Formula (II) nucleating agent [0.87], scavenger [4000], gelatin (1.34)

Layer 10: Interlayer: Titanium dioxide (0.32), gelatin (0.65)

Layer 9: Magenta dye-releaser layer: Magenta RDR (0.43), gelatin (0.86)

Layer 8: Interlayer: Negative silver bromide emulsion (0.05 Ag), scavenger (1.1), gelatin (1.2)

Layer 7: Red-sensitive silver halide layer: Emulsion B (1.34 Ag), Formula (I) nucleating agent [2.0], scavenger [4000], gelatin (1.34)

Layer 6: Gel (0.43) interlayer

Layer 5: Interlayer: Titanium dioxide (0.81), gelatin (0.65)

Layer 4: Cyan dye-releaser layer: Cyan RDR (0.43), gelatin (0.65)

Layer 3: Opaque layer: Carbon (1.9), Cyan RDR (0.02), scavenger (0.03), gelatin (1.2)

Layer 2: Reflecting layer: Titanium dioxide (22.0), gelatin (3.4)

Layer 1: Receiving layer: Mordant (4.8), gelatin (2.3)

The layers were coated on a clear polyester support in the order of numbering.

A control integral imaging receiver of the same layer order arrangement was prepared as above except Layer 7 had Emulsion D at 1.4 g Ag/m².

The following processing pod composition was employed in both units:

Potassium hydroxide	46.8 g/l
4-Methyl-4-hydroxymethyl-1-p-tolyl-3-pyrazolidone	15.0 g/l
5-Methylbenzotriazole	5.0 g/l
Carboxymethylcellulose	46.0 g/l
Potassium fluoride	10.0 g/l
Anionic dispersant (Tamol SN®)	6.4 g/l
Potassium sulfite (anhydrous)	3.0 g/l
1,4-Cyclohexanedimethanol	3.0 g/l
Carbon	191.0 g/l

Two cover sheets each having a timing layer and an acid layer were prepared. The timing layer was coated over the acid layer on a clear polyester support.

The above image transfer film units including the processing composition and cover sheet were used in the following manner:

Each multicolor photosensitive integral imaging receiver was exposed for 1/100 second in a sensitometer through a step tablet to 5000°K illumination (daylight balance-neutral), then processed at a controlled temperature (either 16°C or 22°C) using a viscous processing composition contained in a pod. The processing composition was spread between the IIR and the transparent cover sheet using a pair of juxtaposed rollers to provide a processing gap of about 65 μ m.

After a period of more than one hour the red density of the

stepped image was read. The red minimum density (D_{\min}) and maximum density (D_{\max}) values were read from the above produced sensitometric curve.

The data obtained and tabulated below show higher maximum red dye density at both 16°C and 22°C processing for the tabular grain emulsion. The difference in red D_{\max} at these two temperatures is smaller with the tabular grain emulsion than the octahedral grain check indicating improved processing temperature latitude of the red layer. The speed of the control and example emulsion were essentially equivalent.

Emulsion Type	Red Density		
	D_{\max}/D_{\min} (22°C)	D_{\max}/D_{\min} 16°C	ΔD_{\max}
Octahedral (D) (Control)	1.73/0.22	0.99/0.21	-0.74 (-43%)
Tabular (B) (Example)	1.98/0.36	1.37/0.29	-0.61 (-31%)

Example 1B

The same improved processing temperature latitude and improved D_{\max} at low temperature development are shown in a single color coating with equivalent emulsions.

Coatings similar to those of Example 1A (but Single Color) were made but did not contain layers 15 to 8 (overcoat 16 was coated on top of the red-sensitive silver halide layer, 7). The pod and cover sheet are equivalent to those of Example 1A except the cover sheet had 0.043 g/m² each of inhibitor and competer.

Emulsion Type	Red Density		
	D_{\max}/D_{\min} (22°C)	D_{\max}/D_{\min} 16°C	ΔD_{\max}
Octahedral (D) (Control)	1.66/0.18	0.54/0.18	-1.12 (-68%)
Tabular (B) (Example)	1.80/0.24	1.14/0.21	-0.66 (-37%)

Example 2

This example shows that a coating containing red-sensitized internal latent image-forming tabular grain Emulsion B as used in Example 1A has improved room keeping compared to control octahedral grain Emulsion D.

The example single color coating is the same as the example coating of Example 1B. Two control coatings were employed similar to the control of Example 1B except layer 7 contained 1.4 μ m and 1.8 μ m octahedral emulsions, respectively. The pod and cover sheet were similar to those of Example 1B.

The experimental procedure used was the same as Example 1A except processing was done only at room temperature ($\approx 22^\circ\text{C}$). To evaluate keeping stability one set of coatings was exposed and processed fresh, while another set was exposed and processed after being stored at room temperature for seven weeks.

The data below show that both control coatings using the octahedral grain emulsions lose considerably more D_{\max} after room temperature storage for seven weeks than example Emulsion B. D_{\min} changes (and speed changes) are not significantly different.

Emulsion Type	Red Density		
	D_{\max}/D_{\min} (Fresh)	D_{\max}/D_{\min} (After 7 weeks)	ΔD_{\max}
Octahedral (D) 1.4 μ m	1.62/0.21	1.17/0.16	-0.45 (-28%)
Octahedral (D) 1.8 μ m	1.50/0.20	1.07/0.17	-0.43 (-28%)
Tabular (B)	1.70/0.28	1.50/0.21	-0.20 (-12%)

Example 3

This example shows that single color red-sensitized coatings of tabular grain internal latent image-forming emulsions have both improved reversal speed and rereversal separation when cadmium doped.

The control coating contains an emulsion free of cadmium dopant, Emulsion B, the same as used in Example 1B. The example coating contains an equivalent cadmium doped Emulsion C, as outlined above. The coating structure consists of layers 16, and 7 to 1 as described for Example 1B. The pod and cover sheet are equivalent to Example 1B. The experimental procedure is the same as Example 1A except processing is done only at room

temperature ($\approx 22^\circ\text{C}$). Threshold reversal speeds are read at 0.3 density below D_{\max} , the reversal/rereversal separation is read at 0.7 density. A difference of 30 relative speed units equals 0.30 log E.

The data below show that the cadmium doped emulsion is 0.20 log E faster and has a net speed reversal/rereversal separation of 0.37 log E more than does the corresponding emulsion free of cadmium doping. It is highly desirable that the reversal speed becomes faster and the rereversal speed slower.

Emulsion	Relative Reversal Speed (D = 0.7)	Relative Rereversal Speed (D = 0.7)	Δ
B (non CdII doped)	272	77	195
C (CdII doped)	292	60	232
		(Net gain)	37)

Experimental results have also shown that the surface negative image can be significantly reduced if the shell portion of the tabular grain emulsion is doped with either lead (II) or erbium (III).

Example 4

A high aspect ratio tabular grain internal latent image-forming silver bromide emulsion having an average grain diameter of 5.5 microns, an average grain thickness of 0.12 micron, and an average aspect ratio of 46:1 with the tabular grain accounting for 85 percent of the total grain projected area was prepared.

The emulsion was coated on a polyester film support at 2.15 g/m² silver and 10.4 g/m² gelatin. A second coating was prepared that contained 50 mg/Ag mole 1-(2-propynyl)-2-methylquinolinium bromide. The coatings were exposed for 1/10 second to a 600W 5500°K tungsten light source and processed for 3 minutes at 20°C in a ©Metol (N-methyl-p-aminophenol sulfate)-hydroquinone developer containing 0.25 g/l 5-methylbenzotriazole.

Sensitometric results revealed that the control coating displayed no reversal image. However, the core-shell tabular grain emulsion coating that contained 1-(2-propynyl)-2-methylquinolinium bromide resulted in a reversal image with a D_{\max} of 0.69 and a D_{\min} of 0.18.

This disclosure is applicable to radiographic elements. The preferred radiographic elements of this disclosure are those produced by fully forehardening the radiographic elements having two image-forming layer units located on opposed major surfaces of the support. The interposed support is capable of transmitting radiation to which at least one and, typically, both of the image-forming layer units are responsive. That is, the support is specularly transmissive to exposing radiation. The support is substantially colorless and transparent, even though it can be tinted. The two image-forming layer units each contain at least one radiation-sensitive emulsion containing tabular silver halide grains having an average aspect ratio of greater than 8:1 of the type more specifically described above.

To achieve crossover advantages the tabular silver halide grains have adsorbed to their surfaces spectral sensitizing dye. It is specifically contemplated to employ spectral sensitizing dyes that exhibit absorption maxima in the blue and minus blue — ie, green and red, portions of the visible spectrum. In addition, for specialized applications, spectral sensitizing dyes can be employed which improve spectral response beyond the visible spectrum. For example, the use of infrared absorbing spectral sensitizers is specifically contemplated.

In a preferred form of this disclosure the tabular silver halide grains have adsorbed to their surfaces spectral sensitizing dye which exhibits a shift in hue as a function of adsorption. Any conventional spectral sensitizing dye known to exhibit a bathochromic or hypsochromic increase in light absorption as a function of adsorption to the surface of silver halide grains can be employed in the practice of this disclosure. Dyes satisfying such criteria are well known in the art, as illustrated by T H James, *The Theory of the Photographic Process*, 4th Ed, Macmillan, 1977, Chapter 8 (particularly, F. Induced Color Shifts in Cyanine and Merocyanine Dyes) and Chapter 9 (particularly, H. Relations Between Dye Structure and Surface Aggregation) and F M Hamer, *Cyanine Dyes and Related Compounds*, John Wiley and Sons, 1964, Chapter XVII (particularly, F. Polymerization and Sensitization of the Second Type). Merocyanine, hemicyanine, styryl, and oxonol spectral sensitizing dyes which produce H aggregates (hypsochromic shifting) are known to the art, although J aggregates (bathochromic shifting) is not common for dyes of these classes. Preferred spectral sensitizing dyes are cyanine dyes which exhibit either H or J aggregation.

In a specifically preferred form the spectral sensitizing dyes are carbocyanine dyes which exhibit J aggregation. Such dyes are characterized by two or more basic heterocyclic nuclei joined by a linkage of three methine groups. The heterocyclic nuclei preferably

include fused benzene rings to enhance J aggregation. Preferred heterocyclic nuclei for promoting J aggregation are quinolinium, benzoxazolium, benzothiazolium, benzoselenazolium, benzimidazolium, naphthooxazolium, naphthothiazolium, and naphthoselenazolium quaternary salts.

Although native blue sensitivity of silver bromide or bromoiodide is usually relied upon in the art in emulsion layers intended to record exposure to blue light, significant advantages can be obtained by the use of spectral sensitizers, even where their principal absorption is in the spectral region to which the emulsions possess native sensitivity. For example, it is specifically recognized that advantages can be realized from the use of blue spectral sensitizing dyes. Even when the emulsions of the disclosure are high aspect ratio tabular grain silver bromide and silver bromoiodide emulsions, very large increases in speed are realized by the use of blue spectral sensitizing dyes.

Useful blue spectral sensitizing dyes for high aspect ratio tabular grain silver bromide and silver bromoiodide emulsions can be selected from any of the dye classes known to yield spectral sensitizers. Polymethine dyes, such as cyanines, merocyanines, hemicyanines, hemioxonols, and merostyryls, are preferred blue spectral sensitizers. Generally useful blue spectral sensitizers can be selected from among these dye classes by their absorption characteristics — ie, hue. There are, however, general structural correlations that can serve as a guide in selecting useful blue sensitizers. Generally the shorter the methine chain, the shorter the wavelength of the sensitizing maximum. Nuclei also influence absorption. The addition of fused rings to nuclei tends to favor longer wavelengths of absorption. Substituents can also alter absorption characteristics.

In addition to the features specifically described above the radiographic elements of this disclosure can include additional features of a conventional nature in radiographic elements. Exemplary features of this type are disclosed, for example, in *Research Disclosure*, Vol 184, August 1979, Item 18431. For example, the emulsions can contain stabilizers, antifoggants, and antikink agents, as set forth in Paragraph II, A through K. The radiographic element can contain antistatic agents and/or layers, as set forth in Paragraph III. The radiographic elements can contain overcoat layers, as set out in Paragraph IV. The crossover advantages of Abbott et al can be further improved by employing conventional crossover exposure control approaches, as disclosed in Item 18431, Paragraph V.

Preferred radiographic elements are of the type incorporating at least one higher aspect ratio tabular grain emulsion layer is incorporated in each of two imaging units located on opposite major surfaces of a support capable of permitting substantially specular transmission of imaging radiation. Such radiographic supports are most preferably polyester film supports. Poly-(ethylene terephthalate) film supports are specifically preferred. Such supports as well as their preparation are disclosed in Scarlett US Patent 2,823,421, Alles US Patent 2,779,684, and Arvidson and Stottlemeyer US Patent 3,939,000. Medical radiographic elements are usually blue tinted. Generally the tinting dyes are added directly to the molten polyester prior to extrusion and therefore must be thermally stable. Preferred tinting dyes are anthraquinone dyes, such as those disclosed by Hunter US Patent 3,488,195, Hibino et al US Patent 3,849,139, Arai et al US Patents 3,918,976 and 3,933,502, Okuyama et al US Patent 3,948,664, and UK Patents 1,250,983 and 1,372,668.

The preferred spectral sensitizing dyes are chosen to exhibit an absorption peak shift in their adsorbed state, usually in the H or J band, to a region of the spectrum corresponding to the wavelength of electromagnetic radiation to which the element is intended to be imaged exposed. The electromagnetic radiation producing imagewise exposure is typically emitted from phosphors of intensifying screens. A separate intensifying screen exposes each of the two imaging units located on opposite sides of the support. The intensifying screens can emit light in the ultraviolet, blue, green, or red portions of the spectrum, depending upon the specific phosphors chosen for incorporation therein. In a specifically preferred form of the disclosure the spectral sensitizing dye is a carbocyanine dye exhibiting a J band absorption when adsorbed to the tabular grains in a spectral region corresponding to peak emission by the intensifying screen, usually the green region of the spectrum.

The intensifying screens can themselves form a part of the radiographic elements, but usually they are separate elements which are reused to provide exposures of successive radiographic elements. Intensifying screens are well known in the radiographic art. Conventional intensifying screens and their components are disclosed by *Research Disclosure*, Vol 18431, cited above, Paragraph IX, and by Rosecrants US Patent 3,737,313, the disclosures of which are here incorporated by reference.

To obtain a viewable silver image the photographic or, in preferred applications, radiographic elements are processed in an aqueous alkaline developer or, where the developing agent is incorporated in the photographic element, in an aqueous alkaline activator solution. Development which favors the highest attainable covering power is preferred. As pointed out by James, *The Theory*

of the Photographic Process, cited above, pp 404, 405, and 490, as well as Farnell and Solman, also cited above, the highest levels of covering power result from obtaining the most filamentary developed silver. Direct or chemical development produces comparatively higher covering power than physical development and is therefore preferred. Where silver halide grains are employed that form predominantly surface latent images, it is preferred to employ developers which contain low levels of silver halide solvents — ie, surface developers. It is recognized that covering power is increased by developing over a short time period — that is, at a comparatively high rate. The exposed photographic elements of this disclosure when developed in less than 1 minute and preferably less than 30 seconds to produce a viewable silver image exhibit increased covering power; however, covering power is substantially reduced and bears little relation to grain aspect ratio when development is conducted over eight minutes. To achieve rapid development, it is preferred to employ comparatively vigorous developing agents. Preferred developing agents are hydroquinones employed alone or, preferably, in combination with secondary developing agents, such as pyrazolidones, particularly 3-pyrazolidones such as disclosed by Kendall US Patent 2,289,367, Allen US Patent 2,772,282, Stewart et al UK Patent 1,023,701, and DeMarle et al US Patents 3,221,023 and 3,241,967, and aminophenols, such as p-methylaminophenol sulfate.

Processing techniques of the type illustrated by *Research Disclosure*, Item 17643, cited above, Paragraph XIX, can be employed. Roller transport processing of radiographic elements is particularly preferred, as illustrated by Russel et al US Patents 3,025,779 and 3,515,556, Masseth US Patent 3,573,914, Taber et al US Patent 3,647,459, and Rees et al UK Patent 1,269,268. While the photographic elements of this disclosure are forehardened, they can be used with conventional developers containing prehardeners without any loss in covering power. Since the elements are normally fully forehardened, it is, of course, preferred to entirely eliminate hardeners from the processing solutions. Following development the photographic elements can be fixed to remove residual silver halide by any convenient conventional technique.

Examples 1 through 15

For the purpose of comparing covering power as a function of tabular grain aspect ratio, three tabular silver bromide emulsions according to the present disclosure and a tabular silver bromoiodide prepared according to the teachings of Maternaghan US Patent 4,150,994 having a lower aspect ratio were prepared. The tabular grain emulsion characteristics are set forth below in Table I.

Emulsion	Average Aspect Ratio	Grain		Percent of Projected Area
		Diameter (μm)	Thickness (μm)	
Control Emulsion	3.3:1	1.4	0.42	
Example Emulsion A	12:1	2.7	0.22	>80
Example Emulsion B	14:1	2.3	0.16	>90
Example Emulsion C	25:1	2.5	0.10	>90

Example emulsions A, B, and C were high aspect ratio tabular grain emulsions within the definition limits of this disclosure.

The emulsions were each sulfur and gold sensitized and sensitized to the green portion of the spectrum with spectral sensitizing dye.

The emulsions were then divided into separate samples for hardening. Three samples of each emulsion received 0.5, 1.5, and 4.5 percent by weight, based on the weight of gelatin, respectively, of the hardener bis(vinylsulfonylmethyl) ether (BVSME). Three samples of each emulsion received 0.24, 0.75, and 2.5 percent by weight, based on the weight of gelatin, respectively, of the hardener formaldehyde (HCHO). Three samples of each emulsion received 0.24, 0.75, and 2.5 percent by weight, based on the weight of gelatin, respectively, of the hardener mucochloric acid (MA). Immediately after receipt of the hardener each sample was identically coated on separate, identical poly(ethylene terephthalate) transparent film supports. The emulsion samples were each coated at 200 mg silver per 0.093 dm² and 267 mg gelatin per 0.093 dm².

The unprocessed coated samples were measured for percent swell 7 days after coating, which included 3 days incubation at 38°C at 50 percent relative humidity. Emulsion layer thickness was initially measured, and each sample was then immersed in distilled water at 21°C for 3 minutes. The change in the emulsion

layer thickness was then measured.

Only a portion of each sample was required to perform the swell measurement procedure described above. A remaining portion of each sample was exposed to obtain a maximum density and processed in a conventional radiographic element processor, commercially available under the trademark Kodak RP X-Omat Film Processor M6A-N. Development time was 21 seconds at 35°C. Instead of using the standard developer for this processor, which contains glutaraldehyde as a prehardener, a similar developer of the type disclosed by Example 1 of Barnes et al US Patent 3,545,971 was employed, but the glutaraldehyde prehardener was omitted, and the developer contained no hardener.

At the same level of hardening the photographic elements prepared with the emulsions of the present disclosure exhibited higher covering power and the covering power increase was produced by the higher aspect ratios of the tabular silver bromide emulsions.

For the purpose of comparing crossover as a function of tabular grain aspect ratio, three high aspect ratio tabular grain silver bromide emulsions satisfying the requirements of the present disclosure and a tabular grain silver bromide emulsion having a lower aspect ratio were prepared. The tabular grain characteristics of the emulsions and the average aspect ratio of the tabular grains is set forth below in Table X.

Table X

Emulsion	Cross-over Results	Average Aspect Ratio	Tabular Grain		% of Projected Area
			Diameter (μm)	Thickness (μm)	
Control 1	22.0	7:1	2.5	0.36	>50
Example 1	17.7	12:1	2.7	0.22	>80
Example 2	17.0	14:1	2.3	0.16	>90
Example 3	15.4	25:1	2.5	0.10	>90

Example emulsions 1 through 3 were high aspect ratio tabular grain emulsions within the definition limits of this disclosure.

To obtain a qualitative ranking of the emulsions in terms of crossover performance the emulsions were identically coated on separate, identical poly(ethylene terephthalate) transparent film supports. The emulsions were each coated at 21.6 mg silver per dm² and 28.8 mg gelatin per dm². Prior to coating the emulsions were each identically sensitized to the green portion of the spectrum with a J aggregating dye. The emulsions were forehardened with 1.5% by weight bis(vinylsulfonylmethyl)- ether, based on the total weight of gelatin.

When a radiographic element containing two identical silver halide emulsion layers on opposite sides of a transparent film support is exposed from one side using a screen activated to fluoresce in response to X-ray exposure, identical processing of the emulsion layers does not produce identical characteristic curves. Rather, two laterally offset characteristic curves are produced. The emulsion layer farthest from the exposing screen has been exposed entirely by radiation which has penetrated the nearest emulsion layer and the film support. Thus, the farthest emulsion layer from the screen is exposed entirely by radiation which has 'crossed over'. The average displacement (expressed as Δ log E) between the intermediate portions of the characteristic curves can be used to calculate percent crossover for the radiographic element by using the following equation:

$$(A) \quad \text{Percent Crossover} = \frac{1}{\text{antilog}(\Delta \log E) + 1} \times 100$$

To provide a qualitative ranking of crossover as a function of aspect ratio a characteristic curve was plotted for each directly exposed sample and compared to a second characteristic curve obtained from a sample exposed only to radiation that had passed through the directly exposed sample — i.e., exposed only to crossover radiation. By measuring the average displacement of the intermediate portions of the characteristic curves and employing equation (A) a crossover test result was obtained. The crossover test results reported in Table X show that the tabular silver bromide emulsions of higher aspect ratio useful in the radiographic elements of this disclosure are capable of reducing the percentage of crossover obtained.

Example 4

An emulsion according to the disclosure similar to that of Examples 1 through 3, but having an average aspect ratio of between 12 and 15:1 with an average tabular grain thickness of 0.1 micron, 85 percent by number of the grains of the emulsion being tabular, was coated on both sides of a poly(ethylene terephthalate)

film support. The total silver coverage was 54 mg/dm² on both sides of the support. A sample of the radiographic element was measured for percent absorption as a function of wavelength and found to have a peak absorption at 545 nm.

The Example 4 radiographic element was exposed for 1/50 second in a Macbeth Sensitometer having a 2850°K light source through a Corning 4010 filter to simulate the illumination of a green emitting screen. A test object was interposed between the element and the light exposure source. The test object was of a standard type having a 21 density step scale ranging from 0 to 3.0 density in 0.15 increments. Exposed samples were processed as described above in Examples 1 through 3, except for variations in time and temperature of processing indicated below in Tables XI and XII.

Table XI
Effect of Development Time
on Speed and Contrast

Element	Log Speed ¹			Contrast ²		
	10 sec	21 sec	30 sec	10 sec	21 sec	30 sec
Example 4	337	344	348	3.12	3.36	3.36

Table XII
Effect of Development Temperature
on Speed and Contrast

Element	Log Speed ¹			Contrast ²		
	32°C	35°C	41°C	32°C	35°C	41°C
Example 4	340	344	353	3.30	3.36	3.36

¹ Log Speed is defined by 100 (1-log E), log E being measured at 1.0 above gross fog.

² Contrast was taken as the slope of straight line between two points on the sensitometric curve at 0.2 and 2.0 density above gross fog.

It can be seen from Tables XI and XII that the radiographic element of the present disclosure exhibited little variation in speed and contrast as a function of variations in development times and temperatures. The present disclosure offers significant advantages in processing latitude not afforded by a conventional radiographic element.

Example 5

Two samples of the emulsion according to the disclosure employed in Example 4 were coated on both sides of a support at a total silver coverage of 43 mg/dm². Processing was at 35°C for 21 seconds. In all other respects the description of Example 4 is applicable.

Sensitometric results are summarized in Table XIII below:

Table XIII
Sensitometric Comparison

Element	Ag Coverage (mg/dm ²)	Minimum Density	Maximum Density	Log Speed ¹	Contrast ²
Sample 1 (Example)	43	.18	3.82	347	2.86
Sample 2 (Example)	43	.19	3.79	342	2.82

¹ See Tables XI and XII

² See Tables XI and XII

In reviewing the results reported in Table XIII it can be seen that an acceptable response is being obtained from the radiographic elements of the disclosure, even though the radiographic elements of the disclosure contain a 20 percent reduction in silver coverage as compared to Example 4. In addition the radiographic elements of this disclosure exhibit acceptable crossover characteristics. In this respect this example illustrates that the disclosure is not limited to achieving radiographic elements exhibiting reduced crossover. The radiographic elements of the present disclosure are also capable of permitting reduced silver coverages to be realized without increasing crossover to unacceptable levels. Further, it should be apparent that the advantages of the disclosure can

be realized by any desired combination of reduced silver coverage and reduced crossover.

In some applications it is advantageous to employ thin, intermediate aspect ratio tabular grain silver halide emulsions. Such emulsions can be characterized as containing tabular silver halide grains having a thickness of less than 0.2 micron and an average aspect ratio in the range of from 5:1 to 8:1 accounting for at least 50 percent of the total projected area of the silver halide grains present in the silver halide emulsion.

To provide a specific example of thin, intermediate aspect ratio tabular grain emulsions, the following example is provided relating to a radiographic application. It should, however, be appreciated that these emulsions can be used in other photographic applications.

Control and tabular grain sulfur and gold sensitized emulsions spectrally sensitized with a J-aggregating oxacarbocyanine dye (see Table XIV below for grain characteristics) were coated on both sides of a poly(ethylene terephthalate) film support. Each side contained an emulsion layer of 21.5 mg silver/dm² and 28.7 mg gelatin/dm² with an 8.8 mg gelatin/dm² overcoat. The emulsions were forehardened.

The coatings were exposed to radiation from a Picker Corp single-phase X-ray generator operating a Machlett Dymax Type 59B X-ray tube. Exposure times were 1 second using a tube current of 100 ma and a tube potential of 70 kilovolts. Following exposure the radiographic elements were processed in a conventional radiographic element processor, commercially available under the trademark Kodak RP X-Omat Film Processor M6A-N, using the standard developer for this processor, commercially available under the trademark MX-810 developer. Development time was 21 seconds at 35°C.

The crossover and sensitometric results of the coatings of the control and tabular grain emulsions are reported in Table XIV.

Table XIV

Emulsion No	Grain Diameter	Thickness	Aspect Ratio	Crossover Percent	log Speed*
Control A	0.4 μ m	0.4 μ m	1:1	17.0	0
Tabular 1	0.73 μ m	~0.09 μ m	7.9:1	18.0	105
Tabular 2	0.64 μ m	~0.10 μ m	6.5:1	17.5	99

* 30 speed units = 0.30 log E

The data in Table XIV illustrate the photographic advantage of the thin, intermediate aspect ratio tabular grain silver halide emulsions when coated on both sides of a support and tested in an X-ray format. Control emulsion A had a grain volume of 0.030(μ m)³ and tabular grain emulsion 2 had a grain volume of 0.032(μ m)³. Although both emulsions demonstrated comparable crossover results at near equivalent grain volumes, the tabular grain emulsion was significantly faster in speed (~1.0 Log E). Likewise tabular grain emulsion 1, 0.038(μ m)³ grain volume, had similar crossover to the control emulsion A and was 1.05 Log E faster in speed.

The foregoing discussion of tabular grain silver halide emulsions and photographic applications for these emulsions is intended to be exemplary in nature rather than limiting. To avoid repetition cataloguing of specific combinations generally suggested has been avoided. Although various parameters of the emulsions and their preparation are discussed by reference to numerical ranges, qualitatively similar results can in most instances be obtained beyond the numerical ranges indicated. This disclosure is therefore intended to embrace both what it specifically discloses and what it fairly suggests.

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Heat erasable photographic element and process comprising silver halide background of the invention

This relates to a photographic material, preferably a photothermographic material, comprising photographic silver halide and a combination of components that enables any latent image silver in the material to be erased by a simple uniform heating step prior to imagewise exposure and development of the photographic material.

It has been found that a heat erasable photographic material, preferably a heat erasable photothermographic material, comprises, in reactive association, in a suitable binder, preferably a hydrophilic binder such as gelatin:

- photographic silver halide;
- a mild oxidizing agent which consists essentially of a cobalt

(III) amine salt which upon heating of the photographic material, will oxidize any latent image silver present in the photographic material; and

(c) a weak complexing agent for the oxidized silver.

If the photographic material is a photothermographic material, then a silver halide developing agent, such as a reductive acid, which does not adversely affect the heat erasability and subsequent exposure and thermal processing of the photographic material, is also preferable in reactive association with the silver halide.

A method of producing an image in a heat erasable photographic element, as described, comprises the steps, in sequence:

- heating the element at a temperature and for a time sufficient to erase any latent image silver in or on the photographic silver halide;
- exposing the element resulting from step (A) to light to produce a developable image in the silver halide photographic emulsion layer; then
- developing the image produced in step (B).

A photographic element as described is also useful in thermographic imaging in which the heat erasable photographic silver halide material is uniformly exposed to light followed by imagewise exposure to heat. The imagewise heating step is at a temperature and for a time sufficient to erase any latent image silver in the imagewise heated areas. Optionally, the element after imagewise heating is uniformly exposed to light and then developed, such as by development in an aqueous developer bath or solution.

The heat erasable photographic silver halide material permits the photographic material to be prepared, packaged and handled without the need for darkroom or safelight conditions prior to initial heating of the material.

The heat erasable photographic silver halide material, according to the description, is optionally useful as a renewable photographic material, a reusable photographic material and as a reversal photographic material. For example, the photographic material is optionally useful to record a latent image which is erasable by simply heating the photographic material.

A suitable reducing agent such as ascorbic acid is necessary in the photographic material to provide optimum development during heat processing. Such a reducing agent in the photographic material is not necessary if conventional processing, such as processing in a silver halide developer solution or bath is to be carried out.

A weak complexing agent for oxidized silver is necessary in the photographic silver halide material to produce the desired heat erasing of latent image silver during the initial heating step. Many compounds known in the photothermographic art as thermal solvents, also known as melt formers, are useful in photographic materials as weak complexing agents for oxidized silver. Examples of useful weak complexing agents for oxidized silver are methylurea, 1,3-dimethylurea, urea, hydantoin, succinimide, sulfamide and acetamide. The weak complexing agent for oxidized silver should be selected to avoid adverse effects on the photographic silver halide and other components in the photographic material. For example, N-methylacetamide provides undesired reduction in photographic speed in certain photographic silver halide materials. Useful weak complexing agents for oxidized silver are selected from, for example, those compounds designated as thermal solvents or melt formers described in, for instance, U S Patent 3,438,776 and *Research Disclosure*, October 1976, Item No. 15027. The term "weak" regarding a complexing agent for oxidized silver herein means a degree of complexing strength for silver ion that is less than the complexing strength of sodium thiosulfate and ammonium thiocyanate but that is sufficient to complex silver ion formed in a photographic silver halide material upon initial heating.

The concentration of weak complexing agent for silver ion in the photographic silver halide material should be sufficient to enable heat erasing of latent image silver to occur upon initial heating of the photographic silver halide material. A preferred concentration of weak complexing agent for silver ion is within the range of about 20 mg to about 200 mg per mmole of silver in the photographic material. Optionally, the weak oxidizing agent for silver ion can act as a humectant to increase the level of water in the photographic material which is known to facilitate silver development.

The composition containing the photographic silver halide is prepared by any of the well known procedures in the photographic art, such as described in *Research Disclosure*, December 1978, Item No 17643. The photographic silver halide material optionally contains addenda commonly present in photographic silver halide materials, such as chemical sensitizers, brighteners, antifoggants, emulsion stabilizers, light absorbing or scattering materials, hardeners, coating aids, plasticizers, lubricants and antistatic materials, matting agents, development modifiers and other addenda described in *Research Disclosure*, December 1978, Item No 17643. The photographic silver halide can comprise, for example, internal image photographic silver halide and internally sensitized covered grain silver halide to produce positive images.

The photographic silver halide is optionally spectrally sensitized by means of spectral sensitizing dyes, as described in *Research Disclosure*, December 1978, Item No 17643, combinations of